REMARKS

Reconsideration of the application is requested in view of the modifications above and the remarks below. Claim 2 and 8-14 are pending. Further, Applicants offer evidence in the form of a Declaration (DECLARATION B), submitted herewith, showing that the claimed and cited art referenced products differ.

Rejections under 35 USC 103

1. The Office Action rejects Claims 2, 8-14 are rejected under 35 USC 103(a) as unpatentable over Yanagisawa et al. The rejection should be withdrawn in view of the remarks below.

The rejection does not establish a *prima facie* case of obviousness. It is well settled that to establish a *prima facie* case of obviousness, the USPTO must satisfy all of the following requirements. First, the prior art relied upon, coupled with the knowledge generally available in the art at the time of the invention, must contain some suggestion or incentive that would have motivated the skilled artisan to modify a reference or to combine references. *In re Fine*, 5 USPQ2d 1596, 1598 (Fed. Cir. 1988). Second, the proposed modification must have had a reasonable expectation of success, as determined from the vantage point of one of ordinary skill in the art at the time the invention was made. *Amgen v. Chugai Pharmaceutical Co.* 18 USPQ 2d 1016, 1023 (Fed Cir, 1991), *cert. denied* 502 U.S. 856 (1991). Third, the prior art reference or combination of references must teach or suggest all of the limitations of the claims. *In re Wilson*, 165 USPQ 494, 496. (CCPA 1970). The rejection should be withdrawn in view of the remarks below.

Applicants' invention is directed to an optical data carrier comprising a transparent substrate, a writable information layer applied to a surface of said substrate and an optional reflection layer, said writable information layer containing at least one phthalocyanine dye of the general formula I,

$$\text{CuPc} \begin{cases} (SO_2\text{-}NH\text{-}A\text{-}NR^1R^2)_x \\ (SO_3H)_y \end{cases} \qquad \text{formula I}$$

in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene,

R^1 and R^2, independently represent a member selected from the group consisting of hydrogen, straight chain or branched C_1-C_6 alkylene, substituted C_1-C_6 hydroxyalkyl, and an unsubstituted C_1-C_6 alkyl group, or R^1 and R^2, together with the nitrogen atom to which they are bonded denote a heterocyclic 5- or 6-membered ring , optionally containing another heteroatom

x is 2.0 to 4.0,

y is 0 to 1.5 and

and the sum of x and y is 2.0 to 4.0.

The Office Action alleges that:

Yanagisawa et al. '171 teaches in example 1, the application of a silicon phthalocyanine dye having four sulfoamido groups bound to the phenyl rings of the phthalocyanine moiety in a methanol solution to a polycarbonate substrate to a thickness of 0.2 microns, followed by a gold reflective film and a UV cured resins protective layer and its use as an optical recording medium. *(517-58)*. The use of various metal centers, such as Cu is disclosed. (3/67-68). The substituents may be between 0 and 4 (3/64-66). Useful reflective layers are disclosed. (4/10-18). Useful solvents for the recording film, including tetrafluoropropanol, methanol, diacetone alcohol, 2

ethoxyethanol (CELLOSOLVE) 2-methoxyethanol, and isopherone are disclosed (4/5-9).

It would have been obvious to one skilled in the art to modify the example of Yanagisawa et al. '171 to use a copper metal center, rather than the Si metal center with a reasonable expectation of achieving comparable results based upon the disclosure of equivalence. Further it would have been obvious to use mixtures of the solvents disclosed as useful with these compounds to provide a good coating solution.

Based upon the location of the substituents in the formula and their association (x and y combined add to between two and four), the examiner interprets the coverage to require the recited substitutents to be bound to the phthalocyanine moiety and not the metal (copper).

The applicant argues that the dyes of the claims have significantly improved solubility over those of the prior art and has submitted declaration evidence to support this. The argument concerning the ligands on the central metal is rendered moot by the use of metals such as copper which have fewer coordination sites than silicon. The chemistry of the central metal controls the number of coordination sites, not the formula of Yanagisawa et al. '171. As pointed out by the applicant, copper does not have sufficient coordination sites to bond the hydroxyl moieties, but this is inherent to the metal and the substitution of the copper would be for the silicon and hydroxyl moieties. Dr. Joseph-Walter STAWITZ has submitted a declaration alleging evidence of unexpected results. The examiner holds that the showing is not commensurate in scope with the coverage sought. The examiner notes that the claims embrace $x = 4$ and $y=0$, which is more analogous to the prior art compound III. Clearly a group such as SO_3H, which is able to undergo dissociation would contribute to the dissolution of the compound in a polar solvent. The point of attachment is somewhat vague in the claim as well, which undercuts the applicants arguments concerning ligands on the central metal. The examiner notes that the solvents are not specified in the majority of the claims either, and would require more data to be commensurate in scope with the broad coverage sought. The equivalence of the central metals in the examiner's position still stands and the examiner notes that the comparative data between dyes I and II seem to indicate that the substituents are more important than the central metal, which is different from the argued position of the applicant. (Office Action, page 2 para. 3 through page 4, para. 1).

Yanagisawa et al discloses radicals of the Pc, for example, sulphonamide. However, in the radical disclosed, the metal atom of the Pc must have ligands. In fact, Yanagisawa et al discloses at least one ligand R_1 and/or R_2 (col 3, line 59).

Further, the Office Action alleges that the use of various metal centers such as Cu is disclosed at col 3, line 68. Unfortunately, however, Applicants believe that there is no CuPc known having ligands at the Cu atom. And, there is neither a compound claim nor a process for the preparation of such a compound disclosed therein. Thus, Applicants' believe that the disclosure in Yanagisawa et al was made inadvertently. Further, Yanagisawa et al does not disclose any examples in which the dye has a Cu-atom as a center. Therefore, it would not have been obvious for one skilled in the art to modify Yanagisawa et al and use a copper metal center rather than a Si metal center with a reasonable expectation of achieving comparable results of Applicants' invention.

Applicants' Declaration compared dye I (of Applicants' present invention) with dye III (Yanagisawa et al). Dye III does not contain sulpho groups. The Examiner alleges that the 0.3 SO_3H in Applicants' dye I could improve the solubility compared with a dye, for example, dye III without any SO_3H groups. However, the effect as set forth in the Declaration is not exclusively attributed to the metal center. The Applicants' have compared dye I without SO_3H groups.

From DECLARATION B (Applicants are submitting a copy of the Declaration in which the signature is not clear. Applicants are requesting that the Examiner acknowledge the information from this documents and the Applicants will forward a more clear copy as soon as possible) the number of SO_3H groups within the contested range is irrelevant relative to the properties shown. The comparison with the compound III (Si as metal center) shows that the effect is based alone on the different metal centers.

The Examiner alleges that "[t]he equivalence of the central metals in the Examiners' position still stands and the comparative data between dyes I and II seem to indicate that the substitutents are more important than the central metal, which is different that the argued position of the applicant" (page 3, line last line - page 4, line 2).

However, there is no support for the Examiner's allegation that "the chemistry of the central metal controls the number of coordination sites, not the formula of Yanagisawa et al '171 set for the in the Office Action page 3. Rather, the formula is the only limiting disclosure of Yanagisawa et al and formula I requires two ligands at the metal center. Compounds that have no ligands are not covered by this formula.

2. Claims 2, 8-14 are rejected under 35 USC 103(a) as unpatentable over Miyazaki et al in view of Kovacs et al. The rejection should be withdrawn in view of the remarks below.

The Office Action alleges:

> Miyazaki et al. JP 63-307987 teaches optical recording media embraced by the formula except in examples 1, 8, 13 and 15, but use different metal centers. These are spin coated from Chloroform solutions onto a polymeric substrate.
>
> Kovacs et al. EP 0519395 teaches various central metals, metal oxides and metal chlorides, including Cu. (3/55-57). The use of various solvents is disclosed. (12/29-36). The use of binders is disclosed. (12/37).
>
> It would have been obvious to one skilled in the art to modify the example of Miyazaki et al. JP 63-307987 to use a copper metal center, rather than the metal center of examples 1, 8, 13 and 15 with a reasonable expectation of achieving comparable results based upon the disclosure of equivalence by Kovacs et al. EP 0519395 and the direction to use metals in general by Miyazaki et al. JP 63-307987. Further it would have been obvious to use mixtures of the solvents disclosed as useful with these compounds to provide a good coating solution.
>
> In addition to the basis provided above, the examiner notes that example 1 (V=O), 13 (Ti=O) and 15 (Pb) do not have hydroxyl

> moieties and therefore are not addressed by the data of the applicant. The examiner particularly points to the use of Pb in example 15 which lacks ligands on the central metal. The examiner cites Kovacs et al. to support the equivalence of the central metal and does not suggest the use of the phthalocyanine compounds of Kovacs et al. The comparasion should therefore be with Miyazaki et al. JP 63-307987, not Kovacs et al. EP 0519395. (Office Action, page 4, para 4 through page 5, para. 1).

Miyazaki et al discloses Pc having sulphonamido groups, however no Cu atom is disclosed as metal center as in Applicants' invention. Compounds similar to those of exp.1 and 8h of Miyazaki et al were compared with Applicants' invention of Example 1. Applicants' invention provided a substantially better solubility in the most common solvents used for spin coating processes such that product was completely dissolved (see Declaration, pages 3 and 4, provided herewith). Specifically, the compounds of Miyazaki et al cannot be used for this application technique without causing serious problems in the production line including that the product does not completely dissolve (see Declaration, page 3, provided herewith).

Further, a comparison with the dye having the Pb-metal center of exp. 14 of the table of Miyazaki et al. The respective Pb-dye can not be synthesized. (see DECLARATION B). Further, the enclosed article "Phthalocyanines. Part VII. Phthalocyanine as a Co-ordinating Group. A General Investigation of the Metallic Derivatives" by P. A. Barrett, C. E. Dent, and R. P. Linstead, further confirms that this Pb-dye cannot be formulated. Thus, neither Miyazaki et al nor Kovacs et al, alone or in combination, teach or suggest Applicants' invention. Reconsideration is requested.

3. Claims 2, 8-14 are rejected under 35 USC 103(a) as unpatentable over Yanagisawa et al in view of Sasawaka et al and Nett et al.
The rejection should be withdrawn in view of the remarks below.

The Office Action alleges that:

> Sasakawa et al. '094 who clearly points to the use of solvent mixtures for phthacyanine dye solutions used to cast optical

recording media layers and Nett et al. '064 which teaches copper phthalocyanine dyes having four sulfoamido groups bound to the phenyl rings of the phthacyanine moiety are known to be compatible with various binders, such as cellulosic polymers and that these are soluble in various solvents including those disclosed by Sasakawa et al. '094 which further renders the modification of the examples of Yanagisawa et al. '171 by the use of mixed solvents obvious. (Office Action, page 5, line 19 to page 6, line 3).

However as discussed, Yanagisawa et al the radicals of the Pc may be a sulphonamide, but the metal atom of the Pc must have ligands, at least one (col 3, line 59), and there is no teaching or suggestion of CuPc having ligands at the Cu atom. Thus, Applicants believe that there is no CuPc known having ligands at the Cu atom. there is neither a compound claim nor a process for the preparation of such a compound disclosed therein and that the disclosure in Yanagisawa et al was made inadvertently. Accordingly, one skilled in the art would not modify Yanagisawa et al with the teachings of Nett et al and Sasakawa et al and arrive at Applicants' invention.

Regarding Sasawaka et al, Sasawaka et al discloses a process for the preparation of optical data storage media containing Pcs using special solvents. However, Sasawaka et al does not disclose CuPc of formula 1 of Applicants' invention. Thus, Sasawaka et al does not suggest the dye to be used in the information layer, and specifically not the dye of Applicants' invention. Sasawaka et al in col 3 line 30-40 discloses phthalocyanine, but no CuPc of Applicants' invention is disclosed. Applicants' invention including dye of formula I, is not taught or suggested by Sasawaka et al.

Regarding Nett et al, Nett et al merely discloses surface finishes or printing inks having a pigment including CuPc that are soluble in various solvents. The mere fact that references can be combined or modified does not render the resultant combination obvious unless the prior art also suggests the desirability of the combination. In re Mills, 916 F.2d 680, 16 USPQ2d 1430 (Fed. Cir. 1990). Even though Nett et al may teach various solvents including those disclosed by Sasakawa et al, there is no teaching or suggestion to use the phthalocyanine dyes

of the printing inks and surface finishes in Nett et al in the optical recording layers of Sasakawa et al. Further, there is no teaching or suggestion then to further modify Yanagisawa et al with the solvent. Reconsideration is requested.

4. The Office Action rejects Claims 2 and 8-14 under 35 USC 103(a) as unpatentable over Yanagisawa et al in view of Sasakawa et al and Nett et al and further in view of Lacroix, Crouse and Miyazaki et al. The rejection should be withdrawn in view of the remarks below.

> The Office Action alleges that:
>
> Lacroix et al. '650 teaches phthalocyanine compounds embraced by the claims, but discloses them only for use as dyes, particularly for cellulosic materials such as paper. (Office Action, page 6, para. 4)
>
> The Office Action alleges that:
>
> Crouse '710 teaches phthalocyanine compounds embraced by the claims, but discloses them only for use as dyes, for cellulosic materials. (Office Action, page 6, para. 5)
>
> The Office Action alleges that:
>
> It would have been obvious to one skilled in the art to modify the invention of Yanagisawa et al. '171 as combined with Sasakawa et al. '094 and Nett et al. '064 by using the phthalocyanine dyes taught by Lacroix et al. '650 and Crouse '710 with a reasonable expectation of success based upon their compatability with cellulosic binder materials and the teachings by Miyazaki et al. JP 01-133790 that $-SO_3H$ and $-SO_2NH(CH_2)_3N(C_2H_5)_2$ substituted phthalocyanines are useful in optical recording media. (Office Action, page 7, para 1.)

As discussed, Applicants are submitting DECLARATION B in which the compound of Miyazaki et al does not seem possible to synthesize (Declaration, pages 2-3). Thus, Yanagisawa et al, Sasakawa et al, Nett et al, Miyazaki et al, Lacroix, or Crouse, either alone or in combination, teach or suggest Applicants' invention. Reconsideration is requested

In view of the modifications and remarks above, a Notice of Allowance is earnestly requested.

Respectfully submitted,

By

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It may be concluded that the primverose is coupled with the aglycone in the normal way through the aldehyde group of the sugar. Galiosin was rapidly hydrolysed by the enzymes present in *Primula officinalis*, *P. vulgaris*, and *P. sinensis*, which hydrolyse β-primverosides. Hydrolysis was shown by the colour change from yellow to red and by observing the absorption bands of the aglycone at 5050, 5320, and 4050 A. after its extraction in toluene.

Colour Reactions of Hydroxyanthraquinones.

	Positions of free hydroxyl groups.	Colour in Na_2CO_3.	Colour on aluminium-mordanted silk.
Alizarin	1 : 2	Violet	Red
Quinizarin	1 : 4	Violet	Red
Purpurin	1 : 2 : 4	Purple	Red
Purpurin-3-carboxylic acid	1 : 2 : 4 (CO_2H)	Purple	Red
Xanthopurpurin	1 : 3	Orange	Yellow
Munjistin	1 : 3 (CO_2H)	Orange	Yellow
Galiosin	—	Orange	Yellow

Reduction of Galiosin.—Mitter and Biswas (*loc. cit.*) have shown that purpurin-3-carboxylic acid is reduced by alkaline sodium hyposulphite to munjistin, the 4-hydroxyl group being eliminated. This reaction also took place with galiosin, the sugar residue being removed in the process. The reduction could be made to take place under extremely mild conditions, as with colloidal palladium and hydrogen in neutral solution at 18°. Munjistin was formed quantitatively, and no munjistin glycoside could be found.

Reduction with hyposulphite. Galiosin (50 mg.) and sodium hydrogen carbonate (0·2 g.) in water (10 c.c.) were treated with sodium hyposulphite (0·1 g.) at 19°. After 15 minutes the mixture was shaken in the air, neutralised with dilute sulphuric acid, and extracted with chloroform. On evaporation to dryness a crystalline residue of munjistin (20 mg.) was left, m. p. 229—232° (decomp.).

Reduction with hydrogen and palladium. Colloidal palladium solution (1 c.c. containing 1 mg. of palladium, as prepared by Wohl and Mylo, *Ber.*, 1912, 45, 340) was added to a solution of galiosin (25 mg.) in water (10 c.c.), and hydrogen passed in. After 30 minutes the colour had become much paler and a yellow precipitate had formed. The mixture was extracted with chloroform, from which munjistin (10 mg.) separated, on evaporation to dryness, in rectangular plates, m. p. 220—233° (decomp.), similar in properties to a specimen prepared by the method of Mitter and Biswas (*loc. cit.*). It was soluble in dilute sodium hydrogen carbonate solution, gave an insoluble red barium salt, and decomposed above its m. p., with loss of carbon dioxide, to give xanthopurpurin, m. p. 261°.

Rubiadin Primveroside (V).—This was isolated by the method of Hill and Richter (*loc. cit.*) from *Galium verum*; 500 g. of fresh roots gave 0·7 g. of the *glycoside*, which separated from 50% aqueous alcohol in pale yellow, parallel-sided plates, m. p. 248—250°. The crystals were almost insoluble in cold water, but dissolved on warming. When the aqueous solution was shaken with butyl alcohol, most of the glycoside passed into the butyl alcohol layer. It gave a red insoluble barium salt and a red lead salt, which was precipitated on treatment of the aqueous solution with normal lead acetate and ammonia.

The solution obtained by hydrolysing the glycoside with acid gave the qualitative reactions for a pentose. A micro-pentose estimation by McCance's method with 3·0 mg. of the glycoside gave 24% of pentose. A rubiadin pentosidohexoside would require 27% [Found (micro): C, 56·8; H, 5·1. $C_{26}H_{28}O_{13}$ requires C, 56·9; H, 5·2%].

Hydrolysis. When the glycoside (155 mg.) was boiled with 0·4N-sulphuric acid (15 c.c.) for 6 hours, a flocculent yellow precipitate separated. After several recrystallisations from 97% alcohol this formed yellow needles (60 mg.), m. p. 268°. It was found by mixed m. p. and comparison of solubilities to be identical with the rubiadin-3-glucoside of Schunck and Marschlewski. We are very grateful to Prof. A. Robertson for an authentic specimen of rubiadin-3-glucoside for comparison.

After the hydrolysis and removal of the rubiadin-3-glucoside a pentose was found in the solution. This was identified as $d(+)$-xylose by oxidising it with bromine and isolating cadmium bromoxylonate crystals.

The fact that the rubiadin glycoside gave red salts with alkalis showed that one hydroxyl group in the anthraquinone nucleus was free, and therefore the pentose was attached to the glucose as a disaccharide. Since primverose was isolated from galiosin, it is probable by analogy that this $d(+)$-xylosidoglucoside also was a primveroside. The glycoside was hydrolysed by

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enzymes present in *Primula officinalis* and *P. vulgaris*, from which it follows that the glycosidic linkage was of the β-type.

Rubiadin primveroside has not yet been isolated from madder, but its presence in closely related species suggests that it may be a precursor of the rubiadin-3-glucoside of Schunck and Marschlewski, which was obtained by boiling madder extracts with acid.

It is a pleasure to thank Sir Frederick Hopkins for his encouragement and helpful advice. One of us (D. R.) wishes also to thank the Medical Research Council for a personal grant which was held while a part of the work described was in progress.

THE BIOCHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 29th, 1936.*]

382. *Phthalocyanines. Part VII. Phthalocyanine as a Co-ordinating Group. A General Investigation of the Metallic Derivatives.*

By P. A. BARRETT, C. E. DENT, and R. P. LINSTEAD.

In its power of forming stable derivatives with a wide variety of metals, phthalocyanine can be ranked with acetylacetone. Twenty elements whose phthalocyanine derivatives have been studied are given in the table. This includes representatives of each group (1—8) of the periodic table.

Group 1. (Hydrogen)	2.	3.	4.	5.	6.	7.	8.
Sodium Potassium Copper	Beryllium Magnesium Calcium Zinc Cadmium Barium	Aluminium	Tin Lead	Vanadium	Chromium	Manganese	Iron Cobalt Nickel Platinum

A number of other metallic compounds are still under study, but it seems desirable to indicate the main results which have so far been achieved. Developments in the purely organic chemistry of the group will be described separately.

In one respect the metallic phthalocyanines differ from other organic co-ordination compounds; they are not usually prepared from the parent metal-free compound but from the dinitrile or nitrile-amide of phthalic acid, the metal being fixed at the same time as the phthalocyanine unit is formed (e.g., $4C_8H_4N_2 + Met \longrightarrow C_{32}H_{16}N_8Met$). There is a great tendency, particularly in the case of phthalonitrile, for this to occur and the reactions are exothermic. Metallic reagents suffer an interesting variety of changes in their efforts to provide the metal necessary for phthalocyanine formation. These are illustrated in the summary which follows. A classification based on the valency of the central element has been used.

(1) *Univalent Elements* (H,Na,K).—Free phthalocyanine, $C_{32}H_{16}N_8H_2$ (Byrne, Linstead, and Lowe, J., 1934, 1017), has now been prepared by the decomposition by means of acids or water of the following metallic derivatives: beryllium, sodium, magnesium, potassium, calcium, manganese, cadmium, tin, barium and lead. It is also formed when phthalonitrile is heated at high temperatures either alone or with such catalysts as silica gel or platinum. It has been shown (Dent, Linstead, and Lowe, J., 1934, 1033) that the formula for phthalocyanine is $(C_8H_4N_2)_4H_2$ and not $(C_8H_4N_2)_4$, and independent and conclusive evidence in support of this is given later in this paper. The preparation from phthalonitrile ($C_8H_4N_2$) over platinum in the absence of an obvious reducing agent might appear to favour the second of these formulæ. This objection is not serious because the reaction is accompanied by gross decomposition and deposition of carbon.

The suggestion made in Part III that the formation of free phthalocyanine from phthalonitrile and sodium amyloxide proceeded through the intermediate formation of a sodium compound has been verified. These compounds react in boiling amyl alcohol to yield *disodium phthalocyanine*, which is converted into free phthalocyanine slowly by hot water,

rapidly by dilute acids. The preparation of phthalocyanine from phthalonitrile by this route thus involves the processes :

$$4C_8H_4N_2 + 2NaO{\cdot}C_5H_{11} \longrightarrow C_{32}H_{16}N_8Na_2 \longrightarrow C_{32}H_{16}N_8H_2$$

Experiments designed to determine the fate of the amyloxide residues ($2C_5H_{11}{\cdot}O$) in the first of these reactions were inconclusive.

In attempts made to prepare *N*-methylphthalocyanine from the disodium compound and methyl iodide, no reaction occurred even at 220°. The sodium was rapidly eliminated by a mixture of methyl iodide and ethyl alcohol, but the organic product from the sodium compound was pure unmethylated phthalocyanine. The reaction presumably proceeds as follows :

$$PcNa_2 + 2MeI + 2EtOH \longrightarrow PcH_2 + 2NaI + 2MeOEt$$

[Pc represents the bivalent phthalocyanine group ($C_{32}H_{16}N_8$)].

Potassium amyloxide and phthalonitrile yield a *dipotassium phthalocyanine* similarly but less readily. The metal appears to be more easily removed than is sodium; for example, the salt yields phthalocyanine on treatment with methyl iodide at 170°.

(2) *Elements normally Bivalent* (Be, Mg, Ca, Ba, Pb, Cu, Zn, Cd, Ni, Co).—Massive beryllium is rapidly dissolved by boiling phthalonitrile,* provided that the surface of the metal has first been etched with acid. The product gives on sublimation in a vacuum anhydrous *beryllium phthalocyanine* (PcBe), which yields a *dihydrate* in moist air. Beryllium phthalocyanine is converted into free phthalocyanine when it is dissolved in concentrated sulphuric acid and the solution diluted with water. Magnesium phthalocyanine dihydrate (J., 1934, 1023) has now been dehydrated by careful vacuum sublimation. The *anhydrous* compound is hydrated rapidly and in a characteristic manner in moist air, but can be kept indefinitely in a dry atmosphere. These results confirm the structure previously advanced for the magnesium compound.

Calcium phthalocyanine is conveniently prepared by the action of calcium oxide or ethoxide on phthalonitrile. The reaction with quick-lime presumably involves the oxidation of a small proportion of the nitrile, *e.g.*, by the reaction $76C_8H_4N_2 + 18CaO \longrightarrow 18Ca(C_{32}H_{16}N_8) + 8CO_2 + 2H_2O + N_2$ or an equivalent process. The product is a green insoluble substance which cannot be sublimed and is converted into phthalocyanine by the action of acids. Barium phthalocyanine is formed similarly but less readily from baryta and phthalonitrile. The metal is more easily removed by acids than is calcium.

Copper phthalocyanine may be taken as the prototype of the stable metallic phthalocyanines of normal structure. In addition to the methods already described (Dent and Linstead, J., 1934, 1027), it has been prepared by the action of anhydrous cupric chloride on phthalocyanine in boiling quinoline. This process gave the cupric derivative (PcCu) and there was no indication of the formation of a cuprous compound, $PcCu_2$. Careful fractional crystallisation failed to show the presence of more than one form of the cupric compound. The action of metallic salts on free phthalocyanine is valuable for the preparation of less accessible compounds of this group containing other metals. The smooth formation of cupric phthalocyanine from equivalent amounts of the metal-free compound and cupric chloride confirms the presence in the former of two replaceable atoms of hydrogen.

Zinc phthalocyanine, prepared from the metal and phthalonitrile, resembles the copper compound in many respects. It has the normal structure, PcZn. The substance itself is blue, but when precipitated from its sulphuric acid solution by the addition of water, a greenish-blue sulphate is formed, which regenerates the original substance on treatment with alkali. There is no elimination of metal. A similar salt formation occurs during the reaction between zinc chloride and phthalonitrile. The product contains two atoms of chlorine to the molecule, *i.e.*, to each atom of zinc, and one of these is lost as hydrogen chloride on treatment with sulphuric acid. Dilution of the solution in this acid and

* Thus phthalonitrile, although it contains neither an acidic nor a pseudo-acidic hydrogen atom, dissolves metals to form compounds in which the metallic atoms are held by primary valencies. This is possible because a ring is formed under the conditions of reaction.

neutralisation yields *zinc monochlorophthalocyanine* (which contains one nuclear halogen) and the first product appears to be essentially the *hydrochloride* of this. The original reaction therefore simulates that between cupric chloride and phthalonitrile (Dent and Linstead, J., 1934, 1027), the only difference being that in one case the hydrogen chloride formed by the nuclear halogenation escapes and in the other is fixed as a salt :

$$4C_8H_4N_2 + CuCl_2 = (C_8H_4N_2)_3Cu(C_8H_3N_2Cl) + HCl$$
$$4C_8H_4N_2 + ZnCl_2 = (C_8H_4N_2)_3Zn(C_8H_3N_2Cl)HCl$$

Cadmium phthalocyanine resembles the zinc compound in the method of formation, but differs from it in that it is insoluble and non-volatile, and by the fact that the metal is removed by acids. This significant difference is discussed later.

Nickel phthalocyanine is conveniently prepared from *o*-cyanobenzamide and the metal, but the *cobalt* compound is most easily made by dissolving the etched massive metal in boiling phthalonitrile. These products are normal compounds of the type PcMe; they are stable to concentrated sulphuric acid and sublime well. Cobaltous chloride reacts smoothly with phthalonitrile with the formation of hydrogen chloride and *cobalt monochlorophthalocyanine*. The product yields a mixture of phthalimide and a chlorophthalimide on oxidation and no chloride ion is liberated : hence the chlorine is nuclear. The original reaction thus resembles that between phthalonitrile and cupric chloride.

Lead phthalocyanine is abnormal in many respects. It can readily be prepared by the violently exothermic reaction between litharge and phthalonitrile. The mechanism is probably similar to that suggested above for the reaction between quick-lime and phthalonitrile. The yield is almost theoretical on the basis that one nitrile molecule in 73 is used up in the reduction of the litharge. The product after purification, by either sublimation or crystallisation, corresponds to PcPb and is easily converted into phthalocyanine by the action of mineral acids. It differs from the other normal metallic phthalocyanines in colour (it is bright green), reflex and crystalline form. A mixture of lead sulphate and metal-free phthalocyanine heated under reduced pressure gave a sublimate of lead phthalocyanine, together with a little unchanged free phthalocyanine. This remarkable reaction, which involves the liberation of sulphuric acid or sulphur trioxide, illustrates once more the stability of the phthalocyanine unit. The many peculiarities of lead phthalocyanine are not due to the high atomic weight of the central atom, for the platinum compound is normal.

Other phthalocyanines in which the central metal exhibits bivalency are described below under "elements of variable valency."

(3) *Tervalent Element* (Al).—We expected that the bivalent phthalocyanine complex and an exclusively tervalent atom such as aluminium would interact to form substances of the type Pc·AlX, where X is a univalent atom or group. This was borne out in practice. Aluminium chloride reacted readily with phthalonitrile to yield a metallic phthalocyanine, but as the product is comparatively complex, it will be convenient to consider first the simpler substance obtained from the chloride and free phthalocyanine. These react in boiling quinoline to yield *chloroaluminium phthalocyanine** (PcAlCl), a blue solid which can be purified by crystallisation but decomposes slightly on sublimation. It shows no tendency to hydration but is appreciably soluble in alcohol (abnormal). It dissolves in sulphuric acid with evolution of hydrogen chloride; dilution with water then

* *Note on nomenclature.* Three types of halogen (chlorine in the examples given below) must be distinguished, the chemical differences between which are illustrated in the text. (1) *Nuclear.* When the chlorine atom is substituted in a benzene ring, "chloro" is prefixed to "phthalocyanine" in the name; *e.g.*, the compound from phthalonitrile and cupric chloride is copper chlorophthalocyanine $(C_{32}H_{15}N_8Cl)Cu$. (2) *Central.* When the chlorine is attached to the central metallic atom, "chloro" is prefixed to the name of the metal; *e.g.*, the compound from phthalocyanine and aluminium chloride is chloroaluminium phthalocyanine, $(C_{32}H_{16}N_8)AlCl$. (3) *Saline.* When the chlorine is attached as hydrogen chloride (presumably to a nitrogen atom), "hydrochloride" is added to the name of the compound; *e.g.*, the compound from phthalonitrile and zinc chloride is zinc chlorophthalocyanine hydrochloride, $(C_{32}H_{15}N_8Cl)Zn,HCl$. The nomenclature of other substituted phthalocyanines follows directly from this.

precipitates a greenish-blue sulphate, there being no elimination of metal. Ammonia reacts with this to form *hydroxoaluminium phthalocyanine* (PcAlOH), isolated as a *trihydrate* and a stable *monohydrate*. This substance is amphoteric; it regenerates the sulphate on treatment with sulphuric acid and forms a salt with sodium hydroxide. The reactions involved are:

$$PcH_2 + AlCl_3 \rightarrow PcAlCl + 2HCl$$
$$\text{and}\quad PcAlCl \longrightarrow PcAlHSO_4 \longrightarrow PcAlOH \longrightarrow PcAlONa$$

The formation of the monochloroaluminium compound is strong independent evidence for the presence of two reactive hydrogen atoms in free phthalocyanine.

The water of the monohydrate of the hydroxo-compound can be removed only at very high temperatures; the hydroxyl groups of two molecules then also interact to yield what appears to be *aluminium phthalocyanine oxide*:

$$2PcAlOH,H_2O \longrightarrow (PcAl)_2O + 3H_2O$$

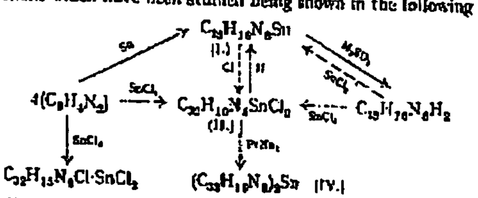
This sublimes in fine needles and shows no tendency to recombine with water. The stable monohydrate appears to illustrate the tendency for aluminium to assume the stable 6-co-ordinate state [PcAl(OH)H$_2$O], but the hydration of other aluminium compounds of the group is irregular.

Aluminium chloride reacts vigorously with phthalonitrile at 250° with evolution of heat and hydrogen chloride to yield *chloroaluminium chlorophthalocyanine*, which readily forms a *dihydrate* and a *trihydrate*. This substance contains chlorine of two dissimilar types. One atom resembles that present in the product from phthalocyanine and aluminium chloride discussed above: it is eliminated by sulphuric acid, and treatment of the product with ammonia yields *hydroxoaluminium chlorophthalocyanine*. The other atom is nuclear and cannot be eliminated. When the molecule is broken up by acid oxidising agents, a mixture of phthalimide and a chlorophthalimide of unknown orientation is produced. The central chlorine atom is not held by an electrovalency, for an alcoholic solution only gives a precipitate very slowly with alcoholic silver nitrate. These compounds are formed by the reactions:

$$4C_8H_4N_2 + AlCl_3 = (C_8H_4N_2)_3(C_8H_3N_2Cl)AlCl + HCl$$
$$C_{32}H_{15}N_8Cl{\cdot}AlCl \longrightarrow C_{32}H_{15}N_8Cl{\cdot}AlHSO_4 \longrightarrow C_{32}H_{15}N_8Cl{\cdot}AlOH$$

The first equation represents the *main* reaction between aluminium chloride and phthalonitrile. The experimental yield of hydrogen chloride was 80% of that required by this equation, but estimation was difficult.

(4) *Elements of Variable Valency* (Sn, Pt, Fe, Mn, Cr, V).—The derivatives of tin provide the only example so far realised in the phthalocyanine group in which the central metal can exhibit both its ordinary states of valency. They have therefore been examined in detail, the reactions which have been studied being shown in the following scheme:



A full arrow indicates that the reaction was realised; a broken arrow that it was realised but that some complication occurred.

Phthalonitrile and metallic tin react slowly at 300° to yield dark blue *stannous phthalocyanine* (I), which is of the normal type, PcSn. Although yielding a blue vapour when heated, it cannot be sublimed satisfactorily. When it is treated with sulphuric acid, the metal is eliminated with the formation of phthalocyanine, but this happens so slowly that side reactions occur and the yield is poor. Stannous phthalocyanine, unlike other phthalocyanines, gives a bright green colour on treatment with nitric acid or nitrogen dioxide corresponding to the conversion of the tin into the stannic state.

The reaction between stannous chloride and phthalonitrile is violently exothermic and gives rise to the green *dichlorotin phthalocyanine* (II) in excellent yield. No hydrogen chloride is evolved and the process involves a unique direct addition. The two chlorine atoms of dichlorotin phthalocyanine are attached to the metal, because (i) oxidative fission yields unchlorinated phthalimide and chloride ion, (ii) caustic alkali and ammonia eliminate the halogen completely, and (iii) if the dichloro-compound were stannous phthalocyanine dihydrochloride, alkali would liberate the parent compound, whereas dichlorotin phthalocyanine would be converted into a dihydroxotin phthalocyanine or an alkali salt of this. The reaction realised was:

$$PcSnCl_2 + 4KOH \longrightarrow PcSn(OK)_2 + 2KCl + 2H_2O$$

so the second alternative is correct.

The action of alkali in alcoholic solution and of sodium ethoxide on the dichloro-compound gave rise to interesting colour changes and gross decomposition of the molecule. Successive treatments with ammonia under pressure and boiling quinoline led to the formation of stannic oxide and free phthalocyanine. The compound is therefore much less stable to alkali than most phthalocyanines.

The interchange between the stannous and the dichlorostannic form is readily effected. When hydrogen is passed through a solution of dichlorotin phthalocyanine in boiling quinoline, reduction to the stannous compound occurs. The reverse reaction is brought about by dry chlorine gas, but is complicated by some nuclear chlorination occurring, and crystallisation of the product yields substantially pure dichlorotin chlorophthalocyanine (III).

When dichlorotin phthalocyanine is boiled with disodium phthalocyanine in chloronaphthalene, sodium chloride is eliminated and *stannic phthalocyanine* (IV) formed. For this compound, which is free from chlorine and oxygen, no other formula seems possible. It is unique in containing two phthalocyanine units attached to a metal. It is more soluble than most phthalocyanines, but the other properties are normal.

By analogy with the reactions already described, it was expected that free phthalocyanine would react with stannous and stannic chlorides in a suitable solvent to yield respectively the stannous and the dichlorostannic derivative. The second of these reactions was realised. The first was complicated by the fact that, although a fixation of tin occurred, the product contained chlorine. Analysis indicated that it might be stannous phthalocyanine hydrochloride, but this awaits confirmation. Stannic chloride reacts with phthalonitrile at 300° to yield the expected *dichlorotin chlorophthalocyanine* (III):

$$4C_8H_4N_2 + SnCl_4 = C_{32}H_{15}ClN_8{\cdot}SnCl_2 + HCl$$

The reaction resembles that between aluminium chloride and phthalonitrile.

In the hope of obtaining dialkyltin phthalocyanines the reactions between dimethylstannic chloride * and free phthalocyanine was examined. The main product was dichlorotin phthalocyanine, methane presumably being eliminated. The reaction between dimethylstannic iodide and phthalonitrile led to gross decomposition.

Platinous chloride combines readily with phthalonitrile to yield *platinum phthalocyanine* (ous), PcPt. This remarkable compound, which contains over a quarter of its weight of platinum, sublimes at about 550° and is stable to sulphuric acid. No nuclear chlorination, either of the product or of the unreacted phthalonitrile, is involved in its formation, hence the chlorine presumably emerges as such or as platinic chloride. There appears to be no reaction between phthalocyanine and platinum metal or platinous chloride.

Iron phthalocyanine, which was the first member of the group studied in these labor-

* For the preparation of these dialkylstannic halides we found the original method of Cahours (*Annalen*, 1860, 114, 367), *viz.*, the direct interaction of tin and methyl iodide, much preferable to that involving the decomposition of methylstannoxylic acid.

atories (J., 1934, 1016; compare B.P. 322,169), could not be obtained pure until the technique of sublimation had been perfected. Material prepared from *o*-cyanobenzamide and metallic iron, after sublimation, gave analytical figures corresponding to *ferrous phthalocyanine*, PcFe. The original iron compound of Part I yielded the same material on sublimation. On oxidation with ceric sulphate (Dent, Linstead, and Lowe, *loc. cit.*) ferrous phthalocyanine takes up oxygen equivalent to 1½ atoms per molecule. This corresponds with the usual oxidation of the complex and the conversion of the iron into the ferric state. Cobalt phthalocyanine behaves similarly, the metal passing into the cobaltic state. Attempts to prepare a chloroiron phthalocyanine (ferric), which would be the "hæmin" of the series, are still in progress. Anhydrous ferric chloride reacts readily with phthalocyanine to form a mixture of the ferric and the ferrous compound, from which the latter was sublimed in good yield.

Black substances of the phthalocyanine class, but of uncertain constitution, are obtained by the interaction of manganese dioxide and phthalonitrile, and of manganese metal and *o*-cyanobenzamide. Both these give *manganese phthalocyanine* (MnPc) on sublimation, and free phthalocyanine on treatment with sulphuric acid. Chromium gives phthalocyanine derivatives with some difficulty and we have not yet obtained substances of certain constitution. Both *o*-cyanobenzamide and phthalocyanine yield compounds of the general type when treated with anhydrous chromous chloride. Vanadium pentoxide reacts with phthalonitrile to yield *vanadyl phthalocyanine*, PcVO, which is stable to sulphuric acid and can be sublimed. As expected on general grounds, no phthalocyanine derivatives of silicon could be obtained from the interaction of silicon tetrachloride with free phthalocyanine. Boron trichloride gave an unstable green compound when heated with phthalocyanine to 300°, which was probably an addition compound. The sharp contrast with aluminium chloride is in agreement with the requirements of the covalency rule, from which it can be predicted that boron cannot give a covalent compound of the type PcBCl.

Discussion.

The question whether the metal atoms of the metallic phthalocyanines are held to the isoindole nitrogen atoms by covalencies or electrovalencies may be examined by applying the tests of volatility and solubility in organic media (Sidgwick, "The Electronic Theory of Valency," 1927, Chapter 6). Sodium, potassium, calcium, barium, and cadmium phthalocyanines differ from the other compounds of the series in being quite insoluble, even on continuous extraction with chloronaphthalene or quinoline above 200°, and incapable of sublimation. The metal–nitrogen link in these compounds must therefore be presumed to be electrovalent and that of all the other metallic derivatives to be covalent. A similar distinction is found among the corresponding metallic acetylacetonates. The five electrovalent metallic phthalocyanines readily liberate metallic ions on treatment with acids or, in some cases, water alone.

The fact that the metal in zinc phthalocyanine is held by covalencies, whereas the corresponding cadmium compound is electrovalent, is in keeping with Fajans' principle that in the same periodic group of metals the tendency to form covalent compounds decreases with rise in atomic number. It is also of interest that, where comparison is possible between pairs of metals in the same group, a metal of higher atomic number enters the phthalocyanine complex more reluctantly and leaves it more readily. This is shown by comparing sodium with potassium, beryllium with magnesium, calcium with barium, and tin with lead.

The stability of metals in metallic phthalocyanines towards acids is not, however, determined only by the tendency of the metal to become ionised, but also by its stability in the planar 4-co-ordinate state and by considerations of molecular dimensions. Robertson (J., 1935, 615; this vol., p. 1195) finds that the distance from the centre of the isoindole nitrogen atoms to the centre of the molecule is 1·91 ± 0·03 A. In free phthalocyanine, and the dimensions are not materially affected by the entry of a metal atom. If we deduct 0·55 as the radius of the nitrogen, there remains a hole in the centre of the molecule of radius about 1·35 A., into which the metal must fit. All the metallic phthalocyanines

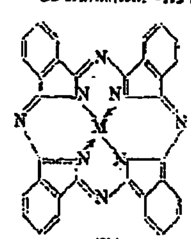
which resist attack by concentrated sulphuric acid actually contain metals whose normal effective radii (as neutral atoms) are of about this order. This is shown in the table, where the atomic radii are those given by Sidgwick ("The Covalent Link in Chemistry," p. 33):

Metal	Cu	Zn	Fe	Co	Ni	Pt	Al (as AlX)	V (as VO)
Radius, A.	1·28	1·31	1·27	1·25	1·24	1·38	1·42	1·30

On the other hand, larger or smaller covalent metals, such as manganese (1·18) and lead (1·73) are displaced by acids. These considerations provide an independent verification of the effective dimensions of the metals given in the table from a novel standpoint.

Klemm and Klemm have recently (*J. pr. Chem.*, 1935, 143, 82) dealt with the magnetic properties of certain metallic phthalocyanines. They conclude from their experiments (i) that the metal atoms in nickel, cobalt and iron phthalocyanines are not held by electrovalencies and (ii) that the metal in the nickel compound is attached to all the isoindole nitrogen atoms. This is in agreement with the views advanced in the present paper, but we do not agree with Klemm and Klemm's suggestion that the metals of magnesium and manganese phthalocyanines are held by electrovalencies because of their comparative lability to acids. Both of these compounds and the beryllium derivative (anhydrous), which also contains a labile metal, are similar in volatility, solubility, and crystalline form to undoubtedly covalent metallic phthalocyanines and we believe their metal–nitrogen links to be covalencies, more easily broken than those of the copper or nickel compounds.

Co-ordination.—As a basis for the discussion of the co-ordination of the metal atoms, we may take the general formula (V) (see J., 1934, 1035; formula XVI) of the normal metallic phthalocyanines, where M is a bivalent metal such as copper, platinum or zinc. There is no chemical evidence incompatible with this formula and it has been strikingly confirmed by the X-ray investigations of J. M. Robertson (*loc. cit.*) and the absolute determination of molecular weights (Robertson, Linstead, and Dent, *Nature*, 1935, 135, 506).



(V.)

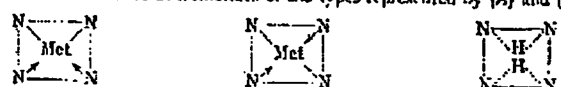
It has been proved that the metal is held to two isoindole nitrogen atoms by primary valencies; its co-ordination with the other two to form four chelate rings (cf. Part VI) is reasonably certain for the following reasons: (*a*) The stability of most of the metallic phthalocyanines towards heat and reagents, particularly mineral acids. There are analogies for this among other compounds recognised as co-ordinated, *e.g.*, cobalt glycine is precipitated unchanged by dilution of its solution in concentrated sulphuric acid (Ley and Winkler, *Ber.*, 1909, 42, 3894; 1912, 45, 372). (*b*) The fact that very few metallic phthalocyanines tend to become solvated during crystallisation. If, for example, the platinum or copper were dicovalent in their phthalocyanine derivatives and not co-ordinated, we should expect them to pass readily into the tetraco-ordinate (or higher) state by combination with two (or more) molecules of a base. These phthalocyanines, however, crystallise unsolvated from bases. (*c*) The existence of metals in so stable a form in the lower state of valency (Fe, Mn) would be remarkable unless the metal were co-ordinated. (*d*) The molecular conditions necessary for co-ordination and chelation are present, namely, lone pairs of electrons on two nitrogen atoms and incomplete outer shells in the central atoms. These atoms are so placed as to permit (one might almost say, to force) ring formation; the four chelate rings are all six-membered, contain one or two double bonds and hence are strainless or practically so (cf. Sidgwick, *op. cit.*, Chapter 14).

Phthalocyanine is therefore a quadridentate chelating unit, capable of occupying four positions in the co-ordination sphere of a metal. This type of four-fold chelation, in which the metal is completely enclosed in an outer ring and the whole molecule thereby knit together, clearly leads to structures of great stability. As usual, this stability is not influenced by the electronic completeness of the core of the metallic atom: zinc phthalo-

cyanine has a rare-gas arrangement (2) (8) (18) 4,4, but the very stable copper compound contains a typical incomplete core, (2) (8) (17) 4,4, as in the cupric ion.

The normal metallic phthalocyanines, Metal Pc, are simply related to the corresponding derivatives of acetylacetone, MetalAc$_n$. Vanadyl phthalocyanine, VOPc, may be compared with vanadyl acetylacetone, and PcSnCl with Ac$_2$SnCl. On the other hand, there are no counterparts of AlAc$_3$ and VAc$_3$. Metals do not exhibit their maximum covalency in their phthalocyanine derivatives, except in the simplest cases, for stereochemical reasons.

Fine Structure.—The general formula (V) for covalent metallic phthalocyanines is not regarded as completely correct, for it implies a distinction between the four nitrogen atoms which hold the metal. We believe that no such distinction exists and that, in Robertson's words, "the o-quinonoid ring does not possess a definite location in the molecule." This follows from Robertson's demonstration of the centrosymmetry of metallic phthalocyanines and from the non-existence of isomerides of the types represented by (A) and (B). Free



(A.) (B.) (C.)

phthalocyanine also is centrosymmetrical, and on classical stereochemistry the two hydrogen atoms should be on opposite sides of the great ring (*trans*). It is preferable to assume that the molecules of phthalocyanine exist in a state of resonance and that each hydrogen atom is co-ordinated with two nitrogen atoms in the manner crudely represented by (C). Independent chemical evidence in support of this has recently come to hand. A similar condition is to be attributed to the metallic derivatives.

Phthalocyanine thus resembles the aromatic type in stereochemistry,* in the loss of unsaturated characteristics and in the very high stability. It appears highly probable that this resemblance originates in a similar, although more complex, resonance in the molecule. A further partial analogy is with the enolic derivatives of unsymmetrical β-diketones and associated substances, which also do not exist in the expected number of isomeric forms and have an abnormal stability (Wheland, *J. Chem. Physics*, 1933, 1, 731; Sidgwick, *op. cit.*). A resemblance between these compounds, including their metallic derivatives, and the aromatic type was recognised 23 years ago by Morgan and Moss (J., 1914, 105, 189).

The considerations advanced here may also be applied to the compounds of the porphyrin group, on the very probable assumption that the Küster-Hans Fischer formula for the fundamental ring structure is correct (compare *Ann. Reports*, 1935, 32, 301).

Experimental.

General Notes on Purification and Analysis.—The methods of crystallisation and sublimation are described below in detail, as it appears that they may be generally useful for the purification of solids only soluble to a small extent in high-boiling liquids and of those capable of sublimation at high temperatures.

1. *Extraction and crystallisation.* The apparatus † is shown in Fig. 1a in a size suitable for the extraction of 2 g. of substance with about 200 c.c. of solvent. The solvent is contained in a 250 c.c. flask of Pyrex glass (A) with a broad fused-on neck, 18" × 2". The solid is placed in an inner vessel of Pyrex glass (B) (6" × 1½"), resembling a drying tube in shape, which contains a layer (C), ½" thick, of Gooch asbestos held between two filter discs. The vessel (B) is held vertically in the neck of the flask by means of four indentations at (D) and can be lowered into or removed from the flask by means of a hook inserted in a hole (E). The liquid is boiled in (A), the vapour passes round (B) and is condensed by means of a condenser (F) mounted in the neck of the flask by a cork carrying a safety tube. The condenser consists of a tube of Pyrex glass terminated by a bulb the end of which is bent at an angle. If chloronaphthalene (b. p. 250°) is used as the extracting liquid, decalin (b. p. about 190°) is used as the liquid in (F). This is boiled by the condensing chloronaphthalene and itself condenses at the top end of (F). The condensed chloronaphthalene drops off the point of (F) and percolates through the solid in (B), which slowly passes into (A). By turning the cork carrying (F) from time to time, the condensing liquid is directed down a different side of (B). The extraction is generally stopped when the separated solid in (A) causes bad bumping. (It was often possible to extract three 2 g. batches of solid with the same solvent before this occurred.) When a lower-boiling solvent is used, the condensing liquid has to be altered to one of suitable b. p., *e.g.*, water for aniline. A water-condenser is then used to cool the top of (F). Direct heating by means of a flame is the most satisfactory. The phthalocyanine crystallises in (A), often from the boiling solution.

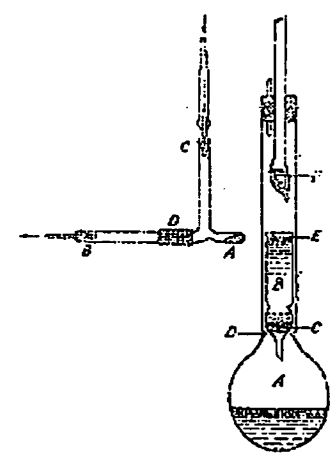


Fig. 1b. Fig. 1a.

Fig. 1a.—*Apparatus for constant extraction with high-boiling liquid.*

Fig. 1b.—*Apparatus for sublimation at high temperatures.*

This extractor is preferable to one of the Soxhlet type, which is difficult to operate with a high-boiling liquid. Extraction proceeds practically at the boiling point and there is no attack of the cork by solvent vapour.

2. *Sublimation.* The apparatus, shown in Fig. 1b, is made from the hardest Jena glass (Supremax). The phthalocyanine is introduced through (B) into the pocket (A), and the tube is then assembled as shown. A stream of dry carbon dioxide enters through a drawn-out capillary at C and escapes to a pump and gauge at B. This prevents sublimation up the vertical arm towards C. The tube at D is kept at about 400° by means of a gauze heated by a small flame. The pressure is suitably adjusted and the phthalocyanine is heated to red heat by a second burner. Volatile impurities pass beyond the gauze towards B, inorganic impurities remain in A, and the phthalocyanine collects at D. At the end of the experiment the sublimate is freed from the glass by means of a bent wire (inserted at C) and carefully removed down the side arm C. For X-ray investigation, crystals over 1 cm. long were prepared in this apparatus.

Phthalocyanines do not melt. Their purity was assessed and they were characterised by microscopic examination (the reflex against a dark ground is often characteristic) and by analysis.* In macro-combustions for carbon and hydrogen all the sublimable substances could be burnt completely in 15 minutes. Nitrogen was estimated by the macro-Kjeldahl method for the aluminium compounds and by macro-Dumas for the remainder. Total chlorine was estimated by fusion with Kahlbaum lime by Liebig's method, a blank determination being necessary. The estimation of metals, where it differs from standard practice, is described under the individual compounds. A few asterisked micro-analyses are by Schoeller.

Phthalocyanine.†—The preparation from the metallic derivatives is described under the individual metals, and the "catalytic" preparation under platinum. Chloronaphthalene is the most convenient solvent for its crystallisation. A sample purified by sublimation had C, 74·0; H, 3·5; N, 22·05 (Calc. for $C_{32}H_{18}N_8$: C, 74·7; H, 3·5; N, 21·8%). Quantitative oxidation of sublimed material with ceric sulphate (J., 1934, 1035) confirmed the presence of 2 atoms of oxidisable hydrogen per molecule.

* See Linstead and Robertson, following paper.

† We gratefully acknowledge Dr. A. R. Lowe's assistance in the development of the technique of crystallisation.

* Measurements of absorption spectra will be described shortly.

† The preparation of free phthalocyanines and of various metallic derivatives from phthalonitriles and o-cyanobenzamides respectively has been described in B.P. 410,814 and 389,182 as well as in the papers already cited. The coloured substances containing iron, nickel and copper made from phthalic anhydride, etc., and ammonia, as described in B.P. 322,169, are now seen to consist of or contain the corresponding phthalocyanines (cf. also B.P. 390,149).

Sodium. 10 G. of phthalonitrile were added to a solution of 1·8 g. of sodium in 100 c.c. of amyl alcohol, and the mixture refluxed gently for 10 minutes. Some ammonia was evolved at first. The product was filtered hot and washed with absolute alcohol and dry ether. *Disodium phthalocyanine* remained as a dull greenish-blue powder with a purple reflex. Yield, 70% (Found: Na, 7·05, 8·0. $C_{32}H_{16}N_8Na_2$ requires Na, 8·2%). It decomposed on being heated under reduced pressure and no appreciable amount of product was removed by extraction with boiling quinoline. A similar preparation was carried out in which only 17 c.c. of amyl alcohol were used. No vapours condensable at − 20° were given off. The amyl alcohol residues yielded impure phthalimide and a trace of (?) isovaleric acid insufficient for identification.

Sodium phthalocyanine on treatment with water at 90° for 15 hours yielded a product containing about 3·6% of sodium. After a further 3 days' treatment the value fell to Na, 0·32, 0·3% and the product yielded phthalocyanine on sublimation. Disodium phthalocyanine did not react with methyl iodide in the cold or at 220° (sealed tube, 4 hours). 5 G. were warmed overnight with 10 c.c. of methyl iodide and 10 c.c. of absolute alcohol. The filtered solid was metal-free phthalocyanine and readily attacked copper in boiling quinoline (Found for sublimed material: C, 75·0; H, 3·8; N, 21·8 (Dumas), 21·7 (Kjeldahl). Calc.: C, 74·7; H, 3·5; N, 21·8%). Sodium phthalocyanine also yielded free phthalocyanine with mineral acids.

Potassium. The preparation of free phthalocyanine through a potassium compound has already been described (B.P. 410,814). The potassium compound was conveniently isolated by refluxing 20 g. of powdered phthalonitrile for an hour with a solution of 5 g. of potassium in 800 c.c. of amyl alcohol. The mixture rapidly became green, but the formation of pigment was slower than in the case of sodium. The product was filtered, washed with dry ether, and dried in a vacuum desiccator. Crude *dipotassium phthalocyanine* was obtained as a blue powder (10 g.) which was insoluble in all solvents and could not be sublimed (Found: K, 11·0, 11·2. $C_{32}H_{16}N_8K_2$ requires K, 13·2%). Prolonged treatment with boiling absolute alcohol led to conversion into free phthalocyanine (ash, 0·3%). 3 G. of the potassium compound were heated at 170° for 6 hours with 5 c.c. of methyl iodide. The product, washed with alcohol and crystallised from chloronaphthalene, was free phthalocyanine (Found: C, 76·0; H, 3·6. Calc.: C, 74·7; H, 3·5%).

Calcium. A mixture of 10 g. of phthalonitrile and 10 g. of quick-lime was heated slowly with mechanical stirring to 275—280°. After 15 minutes the solid mass was exhaustively extracted with boiling alcohol and freed from lime with ice-cold hydrochloric acid. *Calcium phthalocyanine* (70% yield) remained as a dull green pigment almost without lustre. It was insoluble in the usual solvents and could not be sublimed (Found: C, 70·4; H, 3·0; Ca, 5·8. $C_{32}H_{16}N_8Ca$ requires C, 69·6; H, 2·9; Ca, 7·2%). The high carbon and low calcium figure indicate the presence of an impurity of the approximate composition of phthalonitrile, probably the insoluble polymeride previously reported (J., 1934, 1025). A mixture of 20% of $C_8H_4N_2$ and 80% of $C_{32}H_{16}N_8Ca$ requires C, 70·7; H, 2·0; Ca, 6·8%. Extraction with boiling glacial acetic acid, by which the polymeride is slowly dissolved, led to a gradual elimination of calcium. No phthalimide or phthalonitrile was eliminated from the compound by heating at 300° in a vacuum. The calcium content was not lowered by treatment with dilute hydrochloric acid at 0°, but when the compound was dissolved in concentrated sulphuric acid and the solution poured into ice and water, phthalocyanine was precipitated. After crystallisation from chloronaphthalene this had C, 74·4; H, 3·1 (Calc.: C, 74·7; H, 3·5%). The metal was also eliminated when the calcium compound was boiled for 6 hours with 2 vols. of 15% hydrochloric acid (Found: C, 74·1; H, 3·0%). The overall yield of phthalocyanine from phthalonitrile varied from 60 to 68%.

The impure calcium compound was also obtained by refluxing phthalonitrile (10 g.) for 2 hours with a solution of 5 g. of calcium in 50 c.c. of absolute alcohol. After similar purification the product had C, 69·6; H, 3·1; Ca, 5·4%.

Barium. A mixture of 15 g. of phthalonitrile and 7·5 g. of anhydrous baryta was heated at 300° for 2 hours. The reaction was not so vigorous as in the case of quick-lime. The green pigment was freed from excess of nitrile with boiling alcohol but, as it was decomposed by ice-cold dilute hydrochloric acid, the excess of baryta could not be removed. The yield of crude barium compound was 16·5 g.; it was insoluble and could not be sublimed. 10 G. boiled for an hour with dilute hydrochloric acid yielded 7·5 g. of free phthalocyanine (overall yield, 60% from nitrile. Found: C, 74·3; H, 3·4%).

Beryllium. Massive beryllium metal does not react appreciably with phthalonitrile, even after 3 hours' boiling, unless it has first been etched with dilute acid, which presumably removes a film of oxide. Microscopic examination of a lump of metal after reaction shows definite surface pitting. After 2 days a pitted sample again becomes unreactive. 20 G. of phthalonitrile were boiled gently (nitrate bath) with 3 g. of the etched metal. The melt was semi-solid in 30 minutes, and after an hour the product was cooled, the excess metal removed, and the powdered residue washed with alcohol (5·8 g.). On sublimation at about 5 mm. this gave a blue vapour depositing long flattened needles. The lustre appeared more blue and less bronze than that of the metal-free and the copper compound. The main opposite faces of the needle had a bluish lustre and the two less conspicuous faces a bronze lustre (Found: C, 73·8; H, 3·5. $C_{32}H_{16}N_8Be$ requires C, 73·7; H, 3·1%). The crystals broke up in moist air owing to hydration, but less rapidly than those of the magnesium compound. Long crystals of beryllium phthalocyanine become curved and then hook-shaped before finally fracturing to a blue powder. Large crystals sometimes remain intact for as long as 5 hours. The *dihydrate* was a blue powder (Found: C, 69·3; H, 3·5; N, 20·0; Be, 1·6; increase in weight, 6·0. $C_{32}H_{16}N_8Be,2H_2O$ requires C, 68·9; H, 3·6; N, 20·1; Be, 1·6, 1·65; increase in weight, 6·9%.) The original material was soluble to 2·5% in boiling quinoline and to nearly 1% in boiling pyridine. The crystals obtained from these solutions were solvated, as with the magnesium compound (J., 1934, 1026). On treatment with sulphuric acid and dilution in the usual way the beryllium compound yielded phthalocyanine. The elimination of metal was not complete, successive treatments yielding material with Be 0·6 and 0·8%.

[The metal was estimated by slow ashing in an open crucible and weighing as BeO. Micro-determinations gave results about 0·25% too high. High ash values were also obtained by weighing the residue left in the boat after the macro-determinations of carbon and hydrogen. It was first thought that a metallic carbide or nitride was formed under these conditions, but a "wet" carbon analysis of the ash (with chromic anhydride and phosphoric acid) showed the absence of carbon, and a micro-Kjeldahl estimation the absence of nitrogen. The high ash must be due to the presence of a stable hydroxide or peroxide.]

Magnesium. The yield of magnesium phthalocyanine from phthalonitrile and magnesium was improved to 78% and the process quickened by the use of the metal in the form of lightly etched turnings. The product was washed with alcohol and sublimed at 5 mm. There was some decomposition, but the *anhydrous* compound was obtained as lustrous blue needles in 20% yield (Found: C, 71·2 ("wet analysis"). $C_{32}H_{16}N_8Mg$ requires C, 71·6%). The hydration of crystals of the magnesium compound resembled that of the beryllium, but was almost complete in 1 hour in moist air. The product was the dihydrate (Found: C, 66·8; H, 3·3; N, 19·7; Mg, 4·8; increase in weight, 6·0. Calc.: C, 67·1; H, 3·5; N, 19·6; Mg, 4·3; increase in weight, 6·3%). The following experiment proves conclusively that the increase in weight is due to the addition of water and not oxygen. Freshly sublimed magnesium phthalocyanine was sealed in an evacuated tube with two side-arms, one containing phosphoric oxide, the other connected to a reservoir containing water but separated from this by a thin glass diaphragm. The crystals remained in their original state for some days; the limb containing the phosphoric oxide was then sealed off and removed, and the glass diaphragm broken. Within an hour the crystals began to break up in the characteristic manner.

Zinc. Phthalonitrile (10 g.) and zinc dust (1·3 g.) were heated slowly to 145°, by which time the melt had solidified. After 30 minutes at 260—270°, the product was cooled, ground, and washed with alcohol, 9·1 g. of a blue lustrous mass remaining. This sublimed in good yield, the sublimate of *zinc phthalocyanine* resembling the copper compound in appearance (Found: C, 66·8; H, 2·9; N, 19·6; Zn, 11·4. $C_{32}H_{16}N_8Zn$ requires C, 66·5; H, 2·8; N, 19·4; Zn, 11·3%). 1 G. of the unsublimed material was dissolved in sulphuric acid and precipitated in the usual manner. After having been washed with boiling water and alcohol, 1·02 g. of a dull green solid were obtained which turned blue and yielded sodium sulphate when boiled with sodium hydroxide solution. When a similar product was washed with dilute aqueous ammonia, boiling water, and alcohol, blue, substantially pure zinc phthalocyanine (0·87 g.) was obtained (Found: C, 66·8; H, 2·8; Zn, 11·4%).

A mixture of 10 g. of phthalonitrile and 2·7 g. of fused zinc chloride gave a purple-red melt at 150—210°, which turned blue at 240° and soon set to a solid, some hydrogen chloride being evolved. After 20 minutes at 260—270°, the mass was cooled, ground, and washed with alcohol (in which the pigment was slightly soluble). Yield, 9·75 g. (Found: Cl, 9·2. $C_{32}H_{15}N_8ClZn,HCl$ requires Cl, 10·0%). 2·5 G. of this product were dissolved in sulphuric acid (hydrogen chloride was evolved). The green solid precipitated by dilution was washed with alkali and water and dried. 2·08 G. of blue *zinc chlorophthalocyanine* were obtained, which could be crystallised from chloronaphthalene but not sublimed (Found: Cl, 4·6. $C_{32}H_{15}N_8ClZn$ requires Cl, 5·8%). Both this substance and zinc phthalocyanine were slightly soluble in ether.

Cadmium.† 10 G. of phthalonitrile and 2·5 g. of cadmium filings yielded a phthalocyanine readily at 300°. After 2 hours, the product was boiled with alcohol, which removed nitrile and a pink impurity, and was freed from excess of cadmium by repeated flotation in alcohol. *Cadmium phthalocyanine* is dull green, with a purple reflex most noticeable when the substance is moist with organic liquids. It is insoluble in all solvents and cannot be sublimed (Found: C, 63·2; H, 2·5; Cd, 17·6. $C_{32}H_{16}N_8Cd$ requires C, 64·0; H, 2·6; Cd, 18·0%). On treatment with sulphuric acid it yields free phthalocyanine (Found: C, 74·6; H, 3·5%).

Nickel. Phthalonitrile yielded a phthalocyanine (not yet examined) when heated with nickel chloride. 30 G. of *o*-cyanobenzamide were heated in a nitrate bath with 6 g. of nickel foil previously etched with hydrochloric acid. After 2 hours at 270°, the mass was semi-solid and no more ammonia was evolved. The product was cooled, freed from excess of metal, ground, freed from phthalimide with warm 20% sodium hydroxide solution (overnight), and washed with water and boiling alcohol. Yield, 6—8 g. of lustrous crystals. Sublimation gave pure *nickel phthalocyanine* in needles with an extremely bright red lustre. The powder is dull greenish-blue (Found: C, 67·3*; H, 3·0*; N, 19·6*; Ni, 10·4, 10·5. $C_{32}H_{16}N_8Ni$ requires C, 67·2; H, 2·8; N, 19·6; Ni, 10·3%). The unsublimed material passed substantially unchanged through sulphuric acid (Recovery, 92%. Found: C, 66·7; H, 3·0; Ni, 9·5%). [For the determination of nickel, the compound (0·18 g.) was destroyed by the action of 1 c.c. each of concentrated nitric and sulphuric acids; the solution was diluted, nearly neutralised with sodium hydroxide, and the nickel estimated with ammoniacal dimethylglyoxime in the usual way.]

Cobalt. 10 G. of phthalonitrile and 3 g. of etched massive cobalt were refluxed for 4 hours. The product was cooled, freed from metal, boiled with alcohol, and dried (30% yield). *Cobalt phthalocyanine* was unusually soluble in quinoline and chloronaphthalene, giving green-blue solutions, and crystallised readily from pyridine in blue micro-crystals containing combined pyridine, which were washed with ether and dried at 100° (Found: C, 67·1; H, 2·8; N, 19·8; Co, 10·4. $C_{32}H_{16}N_8Co$ requires C, 67·2; H, 2·8; N, 19·6; Co, 10·3%). This sublimed to beautiful blue needles with a reddish-purple lustre (Found: C, 66·7; H, 2·7%). It gave a dark green solution in sulphuric acid, from which it was precipitated unchanged by dilution (Recovery, 70%. Found: C, 66·0; H, 2·8; N, 19·9%). Material which had been treated with sulphuric acid was oxidised quantitatively with ceric sulphate, 1 g.-mol. requiring 1·30, 1·40 g.-atoms of oxygen. Oxidation with boiling nitric acid yielded phthalimide, m. p. 230°.

The same product was obtained from *o*-cyanobenzamide and etched cobalt metal, but the reaction between phthalonitrile and tricobalt tetroxide appeared less satisfactory.

10·2 G. of phthalonitrile were heated to 200° with 2·6 g. of anhydrous cobalt chloride. Pigment was at once formed, the temperature rose rapidly to 250°, and hydrogen chloride was evolved. When the melt had solidified, it was cooled, broken up, and boiled with alcohol. Yield, 85% of a blue powder with a purple lustre, giving green-blue solutions in quinoline and chloronaphthalene and a deep blue solution in pyridine. 3 G. were extracted during 6 hours with 80 c.c. of chloronaphthalene. The solution deposited *cobalt chlorophthalocyanine* (2 g.) in long blue needles with a purple lustre (Found: C, 63·2; H, 2·2; Cl, 6·1. $C_{32}H_{15}N_8ClCo$ requires C, 63·4; H, 2·5; Cl, 5·9%). Crystallisation from pyridine gave a solvated product. Oxidation of the pure compound with boiling nitric acid gave a mixture of imides containing chlorine and melting indefinitely at 200—210°. The mother-liquor gave no reaction for chloride. (Analyses for cobalt were carried out by ashing with nitric acid, then with sulphuric acid, heating to dull redness, and weighing as $CoSO_4$.)

Lead. 10 G. of pure litharge were added in small portions to 20 g. of phthalonitrile at 200°. The mixture frothed and heat was evolved after each addition so that it was advisable to remove the mixture from the heating bath in the early stages. After the addition, heating was continued for 10 minutes and the hard mass was cooled, ground, and washed thoroughly with alcohol. Yield, 29 g. containing about 2 g. of litharge. *Lead phthalocyanine* could be purified by crystallisation from quinoline (Found: C, 53·3; H, 2·2; Pb, 29·2%) or by sublimation, which gave a green vapour. The crystals were fragmented parallelepipeds, pure green by transmitted light; the lustre was dark red and not so evident as that of other metallic phthalocyanines (Found: C, 53·4; H, 2·2; N, 15·0; Pb, 28·5. $C_{32}H_{16}N_8Pb$ requires C, 53·4; H, 2·2; N, 15·6; Pb, 28·8%). (The lead was determined by decomposing the compound with nitric and sulphuric acids and weighing as lead sulphate or by direct ashing with sulphuric acid.)

† Cadmium and vanadyl phthalocyanines have also been prepared by Dr. J. S. H. Davies of Imperial Chemical Industries, Ltd. (private communication).

Treatment of lead phthalocyanine with concentrated sulphuric acid in the usual way gave a mixture of phthalocyanine and lead sulphate, from which most of the sulphate could be removed with ammonium acetate solution. Extraction of the mixture with chloronaphthalene gave pure phthalocyanine in 65% overall yield (Found: C, 74·7; H, 3·6. Calc.: C, 74·7; H, 3·5%). When heated strongly, the mixture regenerated lead phthalocyanine, which sublimed together with a little of the metal-free compound. Crystals of both types could be detected in the sublimate, which contained 22·7% of lead. Crystalline lead phthalocyanine (20 g.) was not apparently affected by concentrated hydrochloric acid, but the addition of an equal volume of water caused the crystals to turn blue immediately without altering in form. The elimination of metal was completed by warming, 14 g. of phthalocyanine being obtained after removal of lead chloride with boiling water.

Treatment of lead phthalocyanine at room temperature for a minute with dilute nitric acid (1 : 1) gave a blue product, from which only free phthalocyanine could be obtained by sublimation. A 25% yield of phthalocyanine could be obtained by successive treatments of the lead compound, contained in a Gooch crucible, with a little concentrated nitric acid, the acid being drawn rapidly by means of a pump into a large volume of water. The nitric acid solution was purple; the precipitate obtained on dilution was first purple, but rapidly changed to the blue of phthalocyanine. When moist nitrogen peroxide was passed over lead phthalocyanine, a similar purple product was formed which subsequently changed to blue. We hope to examine these intermediate products further.

Aluminium. No metallic phthalocyanine was formed by the action of aluminium on phthalocyanine in boiling quinoline.

A mixture of 20 g. (4·8 mols.) of phthalonitrile and 5 g. (1 mol.) of crushed aluminium chloride was heated slowly in a bath to 250°; a sudden reaction then occurred. The internal temperature rose to 300° and the melt solidified and evolved hydrogen chloride. (In a controlled experiment this was led by a current of nitrogen into silver nitrate and was found to be equivalent to 0·8 g.-atom of chlorine per g.-mol. of phthalocyanine formed.) The product was cooled, ground, and washed with benzene. Yield, 20·3 g. 8 G. were crystallised from 400 c.c. of chloronaphthalene, which deposited 5·0 g. of *chloroaluminium chlorophthalocyanine* as a hygroscopic blue powder. Samples once and twice crystallised severally and dried at 115° were analysed (Found: (i) C, 59·4; H, 2·0; N, 17·4; Al, 4·4. (ii) C, 59·7; H, 2·9; N, 17·3. $C_{32}H_{15}N_8Cl{\cdot}AlCl,2H_2O$ requires C, 59·8; H, 3·0; N, 17·4; Al, 4·2%). The total chlorine was determined by the Liebig lime method; the "labile" (non-nuclear) chlorine by oxidation with ceric sulphate, filtration of the imides and estimation of the chloride in the filtrate gravimetrically (Found: total Cl, 11·5; labile Cl, 5·7, 6·1. Calc., 11·0 and 5·5% respectively). Oxidation with nitric and sulphuric acids gave a mixture of phthalimide and a chlorophthalimide, m. p. about 205°, and chloride ion.

Chloroaluminium chlorophthalocyanine was soluble in absolute alcohol (1·0% at room temperature) and also in pyridine, chloronaphthalene, nitrobenzene, acetone and methyl alcohol, but was insoluble in amyl alcohol, ethyl acetate, chlorobenzene and hydrocarbons. Sublimation gave hard blue octahedra in poor yield. These contain labile chlorine, but the composition is uncertain. The dihydrate (above) took up one additional molecule of water from moist air at room temperature, and lost this at 115° (Found: gain in weight, 2·3. Calc., 2·55%). A sample dried at 200° took up 8·2% of water from moist air ($3H_2O$ requires 8·15%) and lost 5·1% (calc., 2·55%) of this at 115°; it then gave the analytical figures required for the dihydrate. The dihydrate *gained* in weight in a calcium chloride desiccator.

An alcoholic solution of the compound gave a precipitate only after 5 hours with alcoholic silver nitrate, but addition of ammonia or alkali removed the labile chlorine and the corresponding hydroxo-compound was precipitated in a finely divided state. This substance was best prepared as follows: 5 G. of the chloro-compound were dissolved in sulphuric acid in the usual way, hydrogen chloride being evolved. Dilution gave a blue-green precipitate (3·4 g.) which contained sulphuric acid. Treatment of this suspension with an excess of aqueous ammonia yielded *hydroxoaluminium chlorophthalocyanine* (3·1 g.). When sodium hydroxide was used, the product contained sodium (Found: Na, 2·1%) removable with difficulty. The hydroxo-compound is blue, insoluble in the usual solvents and in hot concentrated alkali solution, and contains no labile chlorine (Found: C, 64·4; H, 2·7; N, 18·6, 18·6; Al, 4·7. $C_{32}H_{15}N_8Cl{\cdot}AlOH$ requires C, 65·0; H, 2·7; N, 19·0; Al, 4·5%).

Chloroaluminium phthalocyanine. 20 G. of phthalocyanine were boiled with 40 g. of aluminium chloride in 160 c.c. of quinoline for 20 minutes. The original greenish-blue colour rapidly changed to a pure blue. An equal bulk of alcohol was then added; the solution was

boiled and filtered, and the residue washed thoroughly with alcohol. The product, which contained alumina, was extracted in four 11-g. batches with the same 150 c.c. of boiling chloronaphthalene. It was comparatively soluble, each extraction requiring only about 2½ hours. Combined yield, 17·6 g. of blue octahedra (Found: C, 66·3; H, 2·8; N, 19·0; Al, 5·1%). From 12·6 g. of this, 120 c.c. of boiling chloronaphthalene extracted 11·2 g. of analytically pure material in 4 hours (Found: C, 67·2; H, 2·8; Al, 5·0; Cl, 6·8. $C_{32}H_{16}N_8AlCl$ requires C, 66·8; H, 2·8; N, 19·5; Al, 4·7; Cl, 6·2%). This compound showed no tendency to hydrate in moist air.

On treatment with sulphuric acid, hydrogen chloride was evolved, and dilution yielded a bluish-green precipitate. This was filtered off, neutralised with excess of aqueous ammonia, again filtered, washed with boiling alcohol, and dried at 100°. Sintered-glass funnels were essential for these filtrations. *Hydroxyaluminium phthalocyanine (monohydrate)* resembled the corresponding compound containing nuclear chlorine. It was blue, and insoluble in the usual solvents (Found: C, 66·7, 67·2; H, 3·3, 3·3; N, 19·5, 19·0; Al, 5·1, 4·6. $C_{32}H_{16}N_8\text{-}AlOH,H_2O$ requires C, 66·6; H, 3·3; N, 19·5; Al, 4·7%). It was free from chlorine. Sodium hydroxide was taken up immediately from $N/10$-solution, but not in an equivalent amount. In moist air the monohydrate took up a further two molecules of water (Found: gain in weight, 6·1. Calc., 6·0%), which were lost at 100°.

Strong heating of the monohydrate led to the sublimation of *aluminium phthalocyanine oxide* as a blue vapour depositing needles of the usual type. This showed no tendency to combine with water (Found: C, 70·25, 70·05; H, 2·6, 2·8; N, 20·4 *; Al, 4·7. $C_{64}H_{32}ON_{16}Al_2$ requires C, 70·2; H, 2·9; N, 20·5; Al, 4·9%).

The ash left in the boat after the combustion of all the compounds of this group approximates in composition to AlO·OH or Al_2O_3,H_2O (compare the mineral diaspore) and the figures for aluminium given above are calculated on this basis. Thus, four combustions of hydroxyaluminium chlorophthalocyanine (Calc.: Al, 4·5%) gave ashes equivalent to Al, 5·5, 5·5, 5·6 and 5·0% if the ash were taken as Al_2O_3; or to Al, 4·7, 4·7, 4·7, 4·0% if the ash were AlO·OH. Three combustions of aluminium phthalocyanine oxide (Calc.: Al, 4·9%) gave ashes equivalent to 5·6, 5·0, 5·7 (if Al_2O_3) or 4·7, 4·6, 4·9 (if AlO·OH). The ash from each of the latter was treated with nitric acid, ignited in air, and again weighed. Each then gave a value of Al, 4·9% (ash as Al_2O_3), corresponding to the conversion of the oxide into the anhydrous form. Neither of the chloroaluminium phthalocyanines gave satisfactory figures on quantitative oxidation with ceric sulphate.

Tin. A mixture of phthalonitrile (10 g.) and tin (4 g.) was heated at 300° for 3 hours, with mechanical stirring to keep the molten metal in contact with the nitrile. Little phthalocyanine was formed in the first 90 minutes, but the mass then rapidly thickened. The product was cooled, separated from the excess of metal, and exhaustively extracted with alcohol (Soxhlet), a 70% yield of dark blue powder being left. Extraction of this with boiling quinoline first removed a dark impurity, and then *stannous phthalocyanine* was rapidly extracted. It crystallised in dark blue micro-parallelepipeds with a dark violet lustre (Found: C, 60·8; H, 2·5; N, 18·1; Sn, 18·0. $C_{32}H_{16}N_8Sn$ requires C, 60·9; H, 2·5; N, 17·8; Sn, 18·8%). (Tin was estimated by ashing the compound with a drop of concentrated nitric acid, followed by ignition and weighing as stannic oxide.) The dull blue rubbing of this substance changed to bright green when exposed to nitrogen dioxide vapour. Vacuum sublimation gave a deep blue vapour, but only a skin of solid was formed and none of the usual monoclinic needles.

The brown solution of 3 g. of stannous phthalocyanine in 30 c.c. of concentrated sulphuric acid was filtered on to 300 g. of pure crushed ice. A green precipitate was formed which turned blue on the addition of alkali. After 3 hours it was filtered off, washed free from acid, and dried. Recovery, 1·0 g. containing 8·5% of tin. When a solution of the tin compound in sulphuric acid was kept for 4 days before dilution, the elimination of metal was practically complete but the yield of free phthalocyanine (ash, 0·4%) was small.

A mixture of 10 g. of phthalonitrile and 5 g. of powdered anhydrous stannous chloride was heated to 210°. The melt turned green and a violent exothermic reaction occurred, the rise in temperature being 100°; no hydrogen chloride was evolved. The product was cooled, ground, and exhaustively extracted with alcohol. Yield, 90% of a green powder with a fine purple lustre. 3 G. were extracted with boiling quinoline (80 c.c.). The dark earlier extracts were rejected; the pure green solution subsequently obtained deposited *dichlorotin phthalocyanine* (1 g.) as bluish-green plates with a faint purple lustre (Found: C, 54·0; H, 2·2; N, 16·0; labile Cl, 9·9; Sn, 18·5. $C_{32}H_{16}N_8Cl_2Sn$ requires C, 54·8; H, 2·3; N, 16·0; Cl, 10·0; Sn, 16·9%). (Labile chlorine was estimated as follows: a known weight (about 0·2 g.) of the finely powdered

pigment was boiled under reflux in an all-glass apparatus for 24 hours with a solution of 3 g. of potassium hydroxide (chlorine-free) in 50 c.c. of distilled water. The liquid was diluted, the residual pigment filtered off (42 Whatman paper), and the filtrate acidified with nitric acid. After a trace of silica had been filtered off, the chlorine was estimated gravimetrically.) Dichlorotin phthalocyanine dissolved with decomposition in warm concentrated nitric acid; the solution deposited phthalimide (m. p. 230°) and the filtrate contained chlorine ions. The compound dissolved in concentrated sulphuric acid with evolution of hydrogen chloride. A green precipitate was formed on dilution which was turned blue by alkali, the metal being partly eliminated (Found: Sn, 12·0%).

Phthalonitrile reacted readily with stannous iodide at 210°, the temperature rising to 270° and some iodine being evolved. The green product, after extraction with alcohol, appeared to be a mixture of stannous and *di-iodotin phthalocyanine* (Found: I, 23·3. $C_{32}H_{16}N_8I_2Sn$ requires I, 29·0%). This substance lost iodine when boiled with chloronaphthalene or when heated alone.

Dichlorotin phthalocyanine (4 g.) was refluxed for 24 hours with 20 g. of potassium hydroxide in 100 c.c. of water. The product was filtered off, washed free from alkali, and dried. Yield, 3·4 g. of a lustreless blue powder, free from chlorine, mainly the *potassium salt of dihydroxotin phthalocyanine* (Found: C, 51·5; H, 2·4; K, 8·5. $C_{32}H_{16}O_2N_8K_2Sn$ requires C, 51·7; H, 2·2; K, 10·5%). When this was boiled with dilute sulphuric acid, it formed a green sulphate, presumably impure $PcSnSO_4$ (Found: SO_4'', 9·0. Calc., 13·2%).

Dihydroxotin phthalocyanine could not be obtained in a pure condition. When the dichloro-compound was heated under pressure with aqueous ammonia (d 0·88), a dark powder was formed which, when boiled with quinoline, yielded stannic oxide, and free phthalocyanine. Attempts to reduce the dichloro-compound in alkaline media led to the following colour changes: (i) Benzyl alcohol + sodium, faint pink changing to green, stannic oxide deposited. (ii) Ethyl alcohol + sodium, transitory pink changing to bright blue, decolorised by air; stannic oxide deposited, acidification of the filtrate gave phthalic acid (extracted with ether and identified as the anhydride). (iii) Sodium ethoxide and alcoholic potassium hydroxide behaved similarly. Stannous phthalocyanine gave a similar colour change with alcoholic potassium hydroxide, but the pink (magenta) intermediate stage was more clearly marked.

A current of hydrogen was passed for 48 hours through a boiling solution of dichlorotin phthalocyanine (2 g.) in quinoline. The cooled solution deposited stannous phthalocyanine as a crystalline powder with a violet lustre (Found: C, 60·5; H, 2·8%). When hydrogen was passed over the dichloro-compound heated cautiously by means of a free flame, hydrogen chloride was evolved but the residue was partly charred.

Chlorine, dried by means of sulphuric acid and phosphoric oxide, was passed intermittently over a weighed quantity of stannous phthalocyanine. After 3 days the gain in weight was 13·7% (calc. for 2Cl, 11·1%) and the dark crystals had changed to an amorphous green powder. This crystallised from quinoline, in which it was moderately easily soluble, in green plates with a faint lustre (Found: C, 52·8; H, 2·2; labile Cl, 9·7. $C_{32}H_{15}N_8Cl\cdot SnCl_2$ requires C, 52·3; H, 2·0; labile Cl, 9·7%). The analysed compound is therefore essentially *dichlorotin chlorophthalocyanine*, but the gain in weight indicates that the uncrystallised product must have contained some less chlorinated material. Fission of the crystallised product yielded an imide, m. p. 217°, containing chlorine.

Stannic phthalocyanine. 0·5 G. of dichlorotin phthalocyanine and 0·4 g. of disilver phthalocyanine were refluxed in chloronaphthalene for 90 minutes. The colour changed rapidly to a strong dark blue. The solution was kept overnight and filtered. The insoluble portion (discoloured salt) was extracted with water, and yielded 0·10 g. of silver chloride (81%). The chloronaphthalene solution after 5 days' standing deposited a blue crystalline solid which contained solvent of crystallisation. Extraction for 4 days with boiling benzene removed this and left *stannic phthalocyanine* as greenish-blue crystals (Found: C, 67·7; H, 2·9; N, 19·6; Sn, 10·6. $C_{64}H_{32}N_{16}Sn$ requires C, 67·2; H, 2·8; N, 19·6; Sn, 10·35%). This compound sublimes substantially unchanged to give a microcrystalline deposit. It is sufficiently soluble in benzene, xylene and pyridine to give a blue colour in the cold, but it is insoluble in ether, alcohol, acetone, ethyl acetate and light petroleum. Unlike the stannous compound, stannic phthalocyanine gives a normal purple colour with nitrogen dioxide.

A mixture of 5 g. of powdered phthalocyanine, 3 g. of anhydrous stannous chloride, and 50 c.c. of quinoline were refluxed for 12 hours. The cooled solution deposited a solid, which was filtered off and washed with hot alcohol, 3·5 g. of plates with a blue-green lustre being obtained (Found: C, 56·0; H, 2·4; Sn, 18·2%). This contained chlorine. It was boiled for

15 minutes with diluted aqueous ammonia, the appearance being unchanged (Found: C, 57·3; H, 3·5; Cl (total) 5·8%). Crystallisation from quinoline (blue solution) gave small cubes with a reddish lustre (Found: C, 58·0; H, 3·5. $C_{32}H_{16}N_8Sn,HCl$ requires C, 57·5; H, 3·6; Cl, 5·3; Sn, 17·8%). Analysis suggests that this is *stannous phthalocyanine hydrochloride* or *stannous chlorophthalocyanine*. The former constitution is favoured by the method of preparation, the latter by the stability of the halogen.

Free phthalocyanine did not react with boiling stannic chloride (12 hours) and reaction was incomplete after 5 hours at 300°, the product being blue, turned purple by nitrogen dioxide. 5 G. of phthalocyanine were heated for 12 hours at 300° with 5 c.c. of stannic chloride and 5 c.c. of chloronaphthalene. Considerable pressure (hydrogen chloride) was developed in the tube. The green product was washed thoroughly with carbon tetrachloride and ether; crystallisation from quinoline then yielded pure dichlorotin phthalocyanine (Found: C, 55·0; H, 2·4; total Cl, 9·6%). The reaction between phthalocyanine and stannic chloride also appeared to be complete after 24 hours at 300° in the absence of a solvent, for the product was pure green and was not turned purple by nitrogen dioxide.

Phthalonitrile (10 g.) was heated at 300° for 12 hours with 5 c.c. of stannic chloride. The product was partly crystalline but contained a brown impurity, removed by 5 days' extraction with boiling alcohol. The residue was crystallised from quinoline (green solution), which yielded *dichlorotin chlorophthalocyanine* as green crystals with a purple lustre (Found: C, 52·6; H, 2·1; labile Cl, 9·0; total Cl, 14·7. $C_{32}H_{15}N_8Cl{\cdot}SnCl_2$ requires C, 52·2; H, 2·0; labile Cl, 9·7; total Cl, 14·4%).

Experiments with Dimethyltin Dihalides.—The method of Cahours (*loc. cit.*) for the preparation of dimethyltin di-iodide was modified as follows: tin foil (18 g.) was heated with methyl iodide (20 c.c.) at 160° in a sealed tube for 12 hours; the metal had then almost all dissolved and a brown liquid and some needle crystals remained. The product distilled as a pale yellow liquid at 160°/8 mm. The distillation was stopped when a darker brown material began to pass over. The distillate solidified rapidly and, after 3 hours out of contact with air, was dried by means of the pump and on a porous tile. Yield, 40 g. of white crystalline solid, m. p. 42° crude; 43° after crystallisation from light petroleum. The mixture of alcohol and ether used by Cahours for crystallisation leads to darkening.

The dimethylstannic oxide, obtained from 10 g. of the iodide by treatment with sufficient aqueous ammonia, was suspended in 25 c.c. of alcohol and a current of hydrogen chloride was passed until solution was complete. Evaporation left 5 g. of dimethyltin dichloride as white needles, m. p. 107°, identical with material prepared in poor yield by the method of Pfeiffer and Lehnardt (*Ber.*, 1903, 36, 3027) and Pope and Peachey (*Proc. Roy. Soc.*, 1903, 72, 7). The m. p.'s of both the dimethyltin dihalides agree with those given by Pfeiffer (*Z. anorg. Chem.*, 1910, 68, 112), Cahours's values being low.

A mixture of 10 g. of phthalocyanine, 4 g. of dimethyltin dichloride and 10 c.c. of chloronaphthalene was heated for 12 hours at 300°. The finely crystalline product (11 g.), after having been washed with ether, consisted of cubes with a steely-blue lustre and a small amount of material with a purple lustre. The cubes were separated by hand-picking and after being washed with boiling alcohol and benzene yielded dichlorotin phthalocyanine, the lustre changing to purple. The rubbing was green (Found: C, 55·4; H, 2·3; labile Cl, 10·0%).

Phthalonitrile (5 g.) reacted rapidly with dimethyltin di-iodide (2 g.) at 220°, but the product appeared to be badly charred. A little methyl iodide but no iodine or ethane was evolved.

Platinum. A mixture of 1·6 g. of platinous chloride and 20 g. of phthalonitrile was heated to 260° during 20 minutes. Pigment was first formed at about 180° and the melt began to solidify at 230°; some hydrogen chloride was then evolved. The cooled product was ground and thoroughly washed with alcohol. The recovered phthalonitrile was free from chlorine. Yield of residue, 4·2 g., which gave 2·75 g. of crystalline *platinous phthalocyanine*, blue needles with a bronze lustre, from chloronaphthalene. It sublimed readily in small needles [Found: (for crystallised material) C, 54·7; H, 2·0; N, 15·9; Pt, 27·0. (for sublimed) C, 54·4; H, 2·4. $C_{32}H_{16}N_8Pt$ requires C, 54·9; H, 2·3; N, 15·8; Pt, 27·8%]. No chlorine could be detected. Great care was necessary in ashing this compound owing to the ease with which it sublimed. Platinum phthalocyanine is the most resistant member of the group towards oxidation, being comparatively stable to cold nitric acid.

Phthalocyanine failed to react with reduced platinum during 28 hours in boiling quinoline, or with platinous chloride during 6 hours in boiling quinoline. Neither did it react when heated with platinum chloride alone at various temperatures from 300° to 600°. Phthalonitrile reacted with platinous hydroxide (10 hours, 340°) to give a 70% yield of free phthalocyanine (Found:

C, 74·0; H, 3·4; N, 22·0. Calc.: C, 74·7; H, 3·5; N, 21·8%). Heating of 3 g. of phthalonitrile with 0·25 g. of platinum (prepared by ignition of the oxide) for 45 hours at 300° produced some charring and a 70% yield of crystalline phthalocyanine (after extraction with boiling acetic acid). After sublimation, this was ash-free.

Iron. *Ferrous phthalocyanine* was best prepared from *o*-cyanobenzamide, the reaction between phthalonitrile and iron being slow. 20 G. of the cyano-amide were heated at 250° for 6 hours with 4 g. of a pure iron wire, previously etched. The cooled product was freed from phthalimide with concentrated sodium hydroxide solution, the excess of wire removed, and the product filtered off and washed with water and alcohol. Yield, 2·2 g. of lustrous crystals. Crystallisation from quinoline or aniline gave additive compounds, but sublimation gave long needles of the pure ferrous derivative. Both the colour (blue-green) and the lustre are duller than those of the nickel compound (Found: C, 67·4; H, 2·8; N, 19·8. $C_{32}H_{16}N_8Fe$ requires C, 67·6; H, 2·8; N, 19·7; Fe, 9·8%). The same substance was obtained by subliming the product first crystallised from quinoline, solvent of crystallisation being liberated. The sublimed compound was oxidised by ceric sulphate in the manner already described (J., 1934, 1038). 0·1040, 0·1261 G. required 10·75, 13·31 c.c. of $N/30 \times 1·002$ ceric sulphate, whence Fe = 9·7, 9·7% on the basis of the equation

$$2(C_8H_4N_2)_4Fe + 16H_2O + 3O = 8C_8H_5O_2N + Fe_2O_3 + 8NH_3$$

Ferric chloride (A.R., anhydrous) reacted readily with phthalonitrile at 310°, hydrogen chloride being evolved and a good yield of a dark green pigment formed. Although this could be crystallised from chloronaphthalene, no homogeneous product could be isolated and the analytical figures were low for $C_{32}H_{16}N_8Cl{\cdot}FeCl$. It could not be sublimed. Ferric chloride reacted rapidly with phthalocyanine in boiling quinoline. Analysis indicated that the product was a mixture of ferrous phthalocyanine and chloroferric phthalocyanine. It was non-homogeneous under the microscope (Found: C, 66·1; H, 2·9; N, 19·1; Cl, 2·4; Fe, 8·9. A mixture of 60% FePc and 40% FePcCl requires C, 66·0; H, 2·7; N, 19·1; Cl, 2·0; Fe, 9·6%). The chlorine was labile to alkali. Sublimation of the mixture gave a good yield of ferrous phthalocyanine free from chlorine (Found: C, 66·4; H, 2·7; Fe, 9·6%).

Manganese. (i) 30 G. of phthalonitrile and 8 g. of manganese dioxide were heated for 6 hours at 270°. The black amorphous product was ground and washed with benzene (24·8 g.). Extraction of 0·8 g. in small quantities with 110 c.c. of chloronaphthalene gave a deep brown solution, which deposited 5·8 g. of amorphous black solid. (ii) Manganese metal reacted more readily with *o*-cyanobenzamide than with phthalonitrile. 30 G. of the cyano-amide and 8 g. of metallic manganese were heated for 5 hours at 270°. The product was ground and washed with sodium hydroxide solution and alcohol, leaving 18·6 g. of a black solid. Extraction of 10·0 g. with 110 c.c. of chloronaphthalene during 9 hours yielded 4·9 g. of crystalline solid.

The constitution of these products is uncertain. Both gave on sublimation a greenish-black vapour depositing a poor yield of *manganous phthalocyanine* in fine lustrous black needles giving a greenish-black powder (Found: C, 67·2; H, 2·8; N, 19·4. $C_{32}H_{16}N_8Mn$ requires C, 67·7; H, 2·8; N, 19·7; Mn, 9·7%). If the ash left in the combustion boat be taken as Mn_3O_4, the manganese content was 9·7%. Both crude products and the pure manganous compound gave free phthalocyanine on treatment with sulphuric acid, but the yield was comparatively low (25—40%), apparently owing to fission. The free phthalocyanine gave the usual beautiful product on sublimation [Found: C, 74·4; H, 3·6; N, 21·2; (ash, 0·2). Calc.: C, 74·7; H, 3·5; N, 21·8%].

Chromium. No chromium phthalocyanine was formed in the following experiments: phthalocyanine heated in boiling chloronaphthalene with metallic chromium, chromium sesquioxide, phosphate, chromous acetate or with hydrated chromous or chromic chloride; phthalocyanine heated in boiling quinoline with chromous acetate or anhydrous chromic chloride; phthalocyanine sublimed with a mixture with chromium metal, chromium sesquioxide, and chromous acetate.

Anhydrous chromic chloride, prepared by passing chlorine over the finely divided metal at red heat, was converted into chromous chloride by heating in a stream of dry hydrogen until the product was greyish-white and no more hydrogen chloride was evolved. The material was used as soon as possible, as it deliquesced and was oxidised in air.

3 G. of phthalocyanine and 1 g. of chromous chloride were heated in 20 c.c. of boiling quinoline for ½ hour; the liquid was then green. After standing overnight, the solid was filtered off, washed with alcohol (yield, 3·3 g.), and extracted with 120 c.c. of chloronaphthalene. The material extracted in the first 3 hours contained unchanged phthalocyanine and was rejected.

A further 28 hours' extraction removed only 1·66 g. of crystalline material, which corresponded approximately to $C_{32}H_{16}N_8ClCr$. The structure of this is uncertain. It dissolved in sulphuric acid with evolution of hydrogen chloride. Dilution gave a dull green solid, which after neutralisation with aqueous ammonia contained chromium but no sulphur or chlorine, and behaved on analysis approximately as a dihydrate or a hydroxy-monohydrate of chromium phthalocyanine.

o-Cyanobenzamide reacted readily with anhydrous chromous or chromic chloride at 200—270° to give dull green compounds not yet investigated.

Vanadium. A mixture of 2 g. of vanadium pentoxide and 10 g. of phthalonitrile was kept at 240—250° for 30 minutes and then cooled, powdered, and boiled with alcohol (yield, 6 g.). Two successive extractions and crystallisations, chloronaphthalene being used, gave *vanadyl phthalocyanine* as a microcrystalline, blue, lustreless powder (Found : C, 66·1; H, 2·8; N, 19·6; V, 8·5. $C_{32}H_{16}ON_8V$ requires C, 66·4; H, 2·8; N, 19·4; V, 8·9%). The crude product yielded the same substance on sublimation, cubical masses of crystals being deposited from a deep blue vapour (Found : C, 66·1 *; H, 2·0 *; N, 19·6; V, 9·0%). Vanadyl phthalocyanine gave an orange-brown solution in concentrated sulphuric acid, from which it was precipitated unchanged on dilution (Found : V, 9·2%).

Boron, Silicon. 10 G. of disodium phthalocyanine were heated in a pressure tube with 6 g. of boron trichloride. The product, after being washed with carbon tetrachloride, was a bright green powder and was presumably an additive compound, as after 5 minutes in the air of the laboratory or 2 hours in a vacuum desiccator it had changed in colour to a dull blue. Crystallisation of the green product from quinoline gave free phthalocyanine (Found : C, 74·7; H, 3·3%). Elementary boron failed to react with phthalonitrile at 300°. Phthalocyanine did not react with silicon tetrachloride at 300° (Found : C, 74·4; H, 3·7%, in recovered material).

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383. *The Stereochemistry of Metallic Phthalocyanines.*

By R. P. LINSTEAD and J. MONTEATH ROBERTSON.

IT was pointed out by Dent, Linstead, and Lowe (J., 1934, 1037) that the phthalocyanine molecule should lie in one plane, and that co-ordination of a metal normally exhibiting tetrahedral symmetry could only occur by a change either in the configuration of the organic portion of the molecule or in the direction of the valencies of the metal. An X-ray investigation of single crystals of nickel, copper, and platinum phthalocyanines showed that the metal atom and the four surrounding nitrogens lay in one plane (Robertson, J., 1935, 613). The whole molecule of metal-free phthalocyanine has since been proved to be planar to within a few hundredths of an Ångstrom unit (Robertson, this vol., p. 1195).

X-Ray measurements have now been made on single crystals of beryllium, manganese, iron, and cobalt phthalocyanines. These substances are closely isomorphous with phthalocyanine and its copper and nickel derivatives. The cell measurements and crystal data are in the table.

Phthalocyanine derivative.

	(Free.)	Be.	Mn.	Fe.	Co.	Ni.	Cu.	Pt.
At. no. of metal	0	4	25	26	27	28	29	78
a, A.	19·85	21·2	20·2	20·2	20·2	19·9	19·6	23·9
b, A.	4·72	4·84	4·75	4·77	4·77	4·71	4·79	3·81
c, A.	14·8	14·7	15·1	15·0	15·0	14·9	14·6	16·9
β	122·2°	121·0°	121·7°	121·6°	121·3°	121·9°	120·6°	129·6°
Space-group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
Mols. per cell	2	2	2	2	2	2	2	2
Mol. symmetry	Centre	Centre	Centre	Centre	Centre	Centre	Centre	Centre
Vol. of unit cell, A.³	1173	1209	1232	1231	1215	1180	1150	1191
Density (calc.)	1·445	1·43	1·52	1·53	1·53	1·59	1·61	1·97
M	514	521	567	568	571	571	576	707
Electrons per cell, F(000)	532	536	578	580	582	584	590	684

A survey of the reflections from the ($h0l$) zones of the manganese, iron, and cobalt compounds was made by visual inspection of moving-film photographs, taken as nearly as possible under identical conditions. No difference in the intensities of corresponding reflections was observed, and further, they are practically identical with the intensities of the copper and nickel compounds already described. The atomic number of the central metal atom in this series varies from 25 in manganese to 29 in copper, and these atoms make positive contributions to the structure amplitudes, in accordance with the general principles previously given (*idem, ibid.*). Minute differences in the intensities from these compounds must, therefore, exist, but they are too small to be recorded. The similarity of the cell dimensions of these five metallic phthalocyanines shows that the over-all dimensions of the molecules and their relative arrangement in the crystals are practically identical, while the similarity of the intensities shows that the finer details of the structures, including all the interatomic distances and valency angles, must also be practically the same.

Beryllium phthalocyanine is particularly interesting in view of the stereochemistry of the metal atom. The cell dimensions are slightly changed, the a and b axes being longer by a small but measurable amount, with a consequent increase in the molecular volume. The intensities of the ($h0l$) zone are in general very closely similar to those of metal-free phthalocyanine, as might be expected from the low scattering power of the beryllium atom (at. no. 4). A careful inspection, however, reveals a few interesting differences between the two compounds. The (200) plane in beryllium phthalocyanine is represented by a weak reflection, but in the metal-free compound it is absent even on long-exposure films. In beryllium phthalocyanine the (2,0,10), (2,0,$\overline{11}$), and (601) reflections are all a little weaker, and the (60$\overline{7}$), (600), and (20$\overline{2}$) reflections all a little stronger, than the corresponding reflections from metal-free phthalocyanine. These observations can be explained by referring to the phase constants derived for free phthalocyanine (*idem, ibid.*). The (2,0,10), (2,0,$\overline{11}$), and (601) structure factors are of negative sign, whereas the (60$\overline{7}$), (600), and (20$\overline{2}$) are positive. The small positive contribution of the beryllium atom will decrease the amplitude of the negative structure factors, and increase the positive—changes which can be seen in the above reflections, because they are all relatively weak. Such differences as can be observed may therefore be explained by the additional scattering from the beryllium atom. There is no evidence from the intensities (by visual estimate) of any structural change in the molecule due to the presence of the beryllium atom.

The alteration in the cell dimensions noted above, however, shows that there is a small change in the relative positions of the molecules in the crystal. The nature of this change, and whether it is accompanied by any *small* change of structure, may be elucidated by careful measurement and Fourier analysis of the intensities from beryllium phthalocyanine, but in the meantime experimental difficulties prevent such work.

From the standpoint of general stereochemistry, the most important fact which arises is that all the compounds have centro-symmetrical molecules. From this it follows that the metal atoms lie in the same plane as the four nitrogen atoms which carry them. Hence bivalent, 4-co-ordinate beryllium, manganese, iron, cobalt, nickel, copper, and platinum all exhibit planar symmetry in the crystals of their phthalocyanine derivatives.

It is already well established that 4-co-ordinate bivalent platinum exhibits planar symmetry (Cox, J., 1932, 1912; Morgan and Burstall, J., 1934, 1498; Mills and Quibell, J., 1935, 839; Cox, Wardlaw, Webster, *et al.*, J., 1935, 459, 1475; etc.), and it appears that nickel frequently but not invariably occurs in the same condition (Sugden, J., 1932, 246; Cavell and Sugden, J., 1935, 621; Cox, Wardlaw, Webster, *et al.*, *loc. cit.*). The phthalocyanines of these metals are therefore normal. Copper is tetrahedral in the (cuprous) $[Cu(CN)_4]'''$ ion, and may be so in the (cupric) derivative of benzoylpyruvic acid (Mills and Gotts, J., 1926, 3121). The demonstration of the planar distribution of valencies of quadricovalent cupric copper in the phthalocyanine derivative (*loc. cit.*) was followed almost immediately by a similar discovery for the copper derivatives of various diketones (Cox and Webster, J., 1935, 731), and another example has since come to light (Cox, Sharratt, Wardlaw, and Webster, this vol., p. 129). On the other hand, cobalt is tetrahedral in the group $CoCl_4$ (Powell and Wells, J., 1935, 359), and the phthalocyanine deriv-

ative provides the first example of this metal exhibiting planar symmetry. As far as we are aware, nothing has so far been reported on the stereochemistry of 4-co-ordinate bivalent manganese or iron. In the 6-co-ordinate state, iron and cobalt are well known to have an octahedral arrangement of valencies; in the phthalocyanine derivatives, two of these positions become dormant, leaving a planar arrangement.

The most remarkable result is provided by beryllium, for which a tetrahedral symmetry is well established by investigations of its benzoylpyruvic acid derivative (Mills and Gotts, *loc. cit.*) and of its basic acetate (Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, 104, 437).

Pauling's application of wave-mechanics to stereochemistry (*J. Amer. Chem. Soc.*, 1931, 53, 1367) led him to expect a planar distribution of valencies only from transitional elements in which the electrons of the *d* levels were taking part in the formation of valencies. On this basis there is nothing remarkable in the planar arrangement found for iron, cobalt, manganese, and copper. That the very simple atom of beryllium, which normally contains no *d* electrons, should adopt a similar symmetry appears inexplicable on Pauling's theory. It is true that the theoretical difficulty can be avoided by the assumption that in beryllium phthalocyanine the metal is combined with only two nitrogen atoms, but there seems to us no justification for arbitrarily differentiating between this compound and the other covalent metallic phthalocyanines which resemble it so closely in crystalline form. The planar arrangement appears to be very unstable, for the anhydrous beryllium compound readily forms a dihydrate even in moist air (Barrett, Dent, and Linstead, this vol., p. 1720). This behaviour is not paralleled by other phthalocyanines except the magnesium derivative.

It seems highly probable that the molecules of all other covalent metallic phthalocyanines, of the type R, Metal", will be planar. The monoclinic crystals of the zinc and the (anhydrous) magnesium derivative, indeed, appear to be exactly similar to those of the compounds discussed above.

Our general conclusions are (i) that in the metallic phthalocyanines, and probably also in the corresponding porphyrins, the rigid, planar, organic portion of the molecule imposes its steric requirements upon the metal, and (ii) that there is more tolerance in the distribution of valencies about 4-co-ordinate metal atoms than has hitherto been realised.

Finally, it may be pointed out that the stereochemistry of the four *iso*indole nitrogen atoms, which carry the metallic atoms, is novel. The three valencies from each of these lie in one plane and are inclined to each other at approximately 110°, 125°, and 125°. This is only possible owing to the peculiar "aromatic" behaviour of the great ring; if the double and single bonds had fixed positions, the third valency of the imino-nitrogen atoms would be inclined to the general plane.

Experimental.

Single crystals of the metallic phthalocyanines were obtained by low-pressure sublimation in carbon dioxide at about 550° (Barrett, Dent, and Linstead, *loc. cit.*). The specimens selected were in the form of thin laths, with cross sections about 0·3 × 0·1 mm., and several mm. long, with the (001), (100), (201), and (101) faces developed. The *b* axes were measured by rotation photographs about the lath axes with Co-*K*α radiation. The other axial lengths and the β angles were obtained by analysis of moving-film photographs of the (*h*0*l*) zones of reflections, taken on the two-crystal spectrometer.

Anhydrous beryllium phthalocyanine is difficult to handle on account of its hygroscopic nature. Some good crystals were taken directly from the sublimation apparatus and sealed up in thin-walled glass tubes. The lath-like crystal was then shaken to the end of the tube, which was touched with a small flame, causing part of the crystal to melt and fix the remainder in an upright position, suitable for the X-ray work. The glass walls of the tube cause extra scattering of the X-ray beam, and this, combined with the absorption effect, reduces the accuracy of the intensity observations.

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384. *The Preparation of the Ten Dicyanonaphthalenes and the Related Naphthalenedicarboxylic Acids.*

By E. F. Bradbrook and R. P. Linstead.

The main object of this work was the preparation of derivatives of naphthalene from which substances of the type of phthalocyanine could be prepared and by means of which the structure of phthalocyanine could be confirmed. The dicyanonaphthalenes are also interesting because the acids obtained by their hydrolysis serve (more particularly in the form of their crystalline and low-melting methyl esters) as a set of reference substances for the orientation of dialkylnaphthalenes, which are of importance for the determination of the structure of many natural products. The present work acts as a bridge between these hydrocarbons and the well-known naphthylaminesulphonic acids.

Six dicyanonaphthalenes, the 1 : 2-, 1 : 4-, 1 : 5-, 1 : 6-, 2 : 6-, and 2 : 7-isomerides, were already known when the work was commenced. The usual preparative method had been the cyanide fusion of the salts of the appropriate naphthalenedisulphonic acid or chloronaphthalenesulphonic acid. The reported yields were small and our experiments with 1-chloronaphthalene-2-sulphonic acid and naphthalene-1 : 5-disulphonic acid confirmed that these preparative methods were unsatisfactory. We have prepared all the dicyanonaphthalenes, except the 2 : 3-isomeride, from the alkali salts of the corresponding cyano-sulphonic acids by fusion with alkali ferrocyanide or cyanide.* The yields depended in an interesting manner on the relative positions of the two substituent groups and, where comparison was possible, were much better than those obtainable by the old methods. The cyano-sulphonic acids were prepared by the Sandmeyer reaction from the readily accessible naphthylaminemonosulphonic acids.

The average yields of the nine dicyanonaphthalenes from the pure salts of the cyano-sulphonic acids under standardised conditions are shown in the table. The third line gives the yields obtained by the cyanide fusion of the crude products of the Sandmeyer reaction.

Isomeride *	1 : 2	2 : 1	1 : 3	1 : 4	1 : 5	1 : 6	1 : 7	1 : 8	2 : 6	2 : 7
Yield from purified salt	75	70	57	77	53	18 †	31 ‡	9	42	85
Yield from crude salt	60	53	0	69	50	63	24	—	29	45

* The first number denotes the position of the cyano-group.
† The initial material contained inorganic impurity and probably some 1 : 7-isomeride.
‡ The initial material contained inorganic impurity; the yield given is too low.

The reaction appears to be governed by the following rules: (1) There is no difference between the ease of replacement of an α- and a β-sulpho-group by a cyano-group (compare the 1 : 2- and 2 : 1-salts). (2) Reaction is favoured when the sulpho- and the cyano-group are separated by an even number of nuclear carbon atoms (compare the 1 : 2-, 1 : 4-, 1 : 5-, 1 : 7-, and 2 : 6- with the 1 : 3-, 1 : 6-, 1 : 8-, and 2 : 7-salts). (3) When the two groups are separated by an even number of nuclear carbon atoms and are in the same ring, the reaction is independent of the number of carbon atoms (1 : 2-, 2 : 1- and 1 : 4-); but when the groups are in different rings, the yields fall off (1 : 5-, 1 : 7-, 2 : 6-). There appears to be an activation of the sulpho-group by the cyano-group which is transmitted by means of a double bond or conjugated system of double bonds. In the present state of our knowledge of high-temperature reactions of this type it would be premature to define this more exactly.

As 2-naphthylamine-3-sulphonic acid was not accessible, 2 : 3-dicyanonaphthalene was prepared from 2-amino-3-naphthoic acid. The compound $C_{12}H_7O_2N$, m. p. 273°, obtained by treating the diazotised amino-acid with potassium cuprocyanide and subliming the product was shown to be, not 2-cyano-3-naphthoic acid as suggested by Waldmann (*J. pr. Chem.*, 1930, 128, 150), but the isomeric imide of naphthalene-2 : 3-dicarboxylic acid

* One reaction of this type has previously been reported: Weissgerber and Kruber obtained 1 : 6-dicyanonaphthalene from potassium 2-cyanonaphthalene-5-sulphonate in 25% yield (*Ber.*, 1919, 52, 346).

(Freund and Fleischer, *Annalen*, 1913, 402, 67). The analogous conversion of *o*-cyanobenzoic acid into phthalimide by the action of heat has been observed by Hoogewerf and van Dorp (*Rec. trav. chim.*, 1892, 11, 91). When 2 : 3-naphthalimide was passed over thoria at 460° in a current of ammonia, it yielded 2 : 3-dicyanonaphthalene (compare Reid and collaborators, *J. Amer. Chem. Soc.*, 1916, 38, 2128; 1931, 53, 321).

The melting points of the nitriles and the methyl esters obtained from them in the usual way are tabulated below:

Isomeride	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6	1 : 7	1 : 8	2 : 3	2 : 6	2 : 7
M. p. of dinitrile	190°	179°	208°	263°	211°	197°	272°	251°	303°	267°
M. p. of methyl ester	85°	—	67°	119°	98°	100°	104°	47°	190°	135°

Where comparison is possible, these figures are in substantial agreement with those in the literature. Ruzicka and van Melsen (*Helv. Chim. Acta*, 1931, 14, 404) gave m. p. 86—87° for the methyl ester of the 1 : 7-acid prepared from 1-methyl-7-ethylnaphthalene (Harvey, Heilbron, and Wilkinson, J., 1930, 423). The figure given above confirms the orientation of this hydrocarbon. Darmstaedter and Wichelhaus (*Annalen*, 1869, 152, 307) prepared four dicyanonaphthalenes of uncertain orientation. The first, m. p. 204°, was obtained by cyanide fusion of the monosulphonic acid prepared by sulphonating α-bromonaphthalene. Weissgerber and Kruber (*loc. cit.*) have suggested that this is identical with their 1 : 5-dicyanonaphthalene, m. p. 209°, but the 5-sulphonation implied is unacceptable and the present work confirms that this dinitrile and the parent bromosulphonic acid have the 1 : 4-orientation adopted in Beilstein's "Handbuch." From the melting points of the other dinitriles of Darmstaedter and Wichelhaus and on general grounds we think it probable that (1) the acid obtained by the bromination of naphthalene-α-sulphonic acid, which gives a dinitrile, m. p. 236°, is crude 6-bromonaphthalene-1-sulphonic acid; (2) the corresponding bromo-acid from naphthalene-β-sulphonic acid (dinitrile, m. p. 170°) is a mixture of 5- and 8-bromonaphthalene-2-sulphonic acids, mainly the latter; (3) the dinitrile, m. p. 262° from Darmstaedter and Wichelhaus's naphthalenedisulphonic acid (prepared in an unspecified way) is the 1 : 5-isomeride.

The present work makes naphthalene-1 : 2-, -1 : 4-, -1 : 5- and -2 : 6-dicarboxylic acids comparatively accessible for synthetic purposes.

Experiments on the conversion of the dicyanonaphthalenes into benzaphthalocyanines are described in the following paper.

Experimental.

1 : 2-*Series*.—(1) Commercial sodium 1-naphthylamine-2-sulphonate gave as good results as material purified through the calcium salt (Erdmann, *Annalen*, 1893, 275, 226). There was no detectable contamination by the 1 : 4-isomeride. The moist diazo-compound (Cleve, *Ber.*, 1892, 25, 2475) from 80 g. of the salt was added during 45 minutes to a stirred solution of 108 g. of copper sulphate and 117 g. of potassium cyanide in 600 c.c. of water at 60—80°. After a further 30 minutes at this temperature, 45 g. of sodium chloride were added, the sodium 1-cyanonaphthalene-2-sulphonate (A) was filtered off from the cooled solution and dissolved in very dilute hydrochloric acid, and the potassium salt precipitated by the addition of potassium chloride. This formed pinkish plates from alcohol. Yield, 57 g. (64%) (compare Friedländer and Woroschzoff, *Annalen*, 1912, 388, 7).

After many preliminary experiments the following general process was used for the cyanide fusion of this salt and its isomerides (compare Brit. Pat. 436,661). A mixture of 25 g. of the cyano-sulphonate and 40 g. of anhydrous potassium ferrocyanide (*ca.* 5 equivs.) was contained in the central portion of a tube of Pyrex glass, 24" by 1½", enclosed in an electric furnace 12" long. One end of the tube was connected to a source of carbon dioxide, the other to a receiver, manometer and pump. The tube sloped very slightly towards the receiver. A slow stream of carbon dioxide was passed, the pressure reduced to about 40 mm., and the temperature raised slowly until a sublimate of dicyanonaphthalene appeared on the cold part of the tube. The temperature was gradually raised as the rate of formation of the product decreased and the process was generally complete in 1—2 hours. The dicyanonaphthalene sublimed in an almost pure condition and no more could be isolated by reheating the residue or extracting it with benzene. The success of the reaction depended upon the efficient transmission of heat through

the mass. In the 1 : 2-series a 10 g. batch gave the best yield (75%) and this diminished with batches above 25 g. Addition of metal turnings to conduct the heat led to a slight decrease in the yield, as some pigment of the phthalocyanine type was formed. The reaction occurred at 320—370° with the 1 : 2-cyano-sulphonate and most of its isomerides. Anhydrous sodium and potassium ferrocyanide and sodium cyanide were about equal as reagents; potassium cyanide reacted equally well but at a higher temperature, probably owing to the difference in fusion points. The use of a eutectic mixture of cyanides and the preheating of the carbon dioxide were without advantage. Potassium thiocyanate was unsuitable both as a reagent and as a flux. If potassium ferrocyanide was used in slight excess, the reaction did not proceed so readily but the yield was unaffected; a large excess was without advantage. The ferrocyanide was conveniently dehydrated in the same apparatus at 200°.

Sodium cyanonaphthalenesulphonates were equivalent to the potassium salts. The crude product from the Sandmeyer reaction (such as A above) could be used with advantage for preparative purposes. The overall yield of 1 : 2-dicyanonaphthalene from sodium 1-naphthylamine-2-sulphonate was constant at *ca.* 40% irrespective of the purification of the intermediate.

(2) 200 G. of commercial Tobias acid (2-naphthylamine-1-sulphonic acid) were suspended in hot water and neutralised with sodium carbonate, and the solution filtered, acidified, and cooled. The precipitated acid was crystallised from water, just neutralised with sodium hydroxide, and cooled. β-Naphthylamine was filtered off, and the salt of the amino-acid in the filtrate diazotised either by the method used for naphthionic acid by Erdmann (*Annalen*, 1888, 247, 320) or by that of Cleve (*loc. cit.*). The diazo-compound was converted into *sodium 2-cyanonaphthalene-1-sulphonate* by the method already described. Yield, 92% of crude salt, which formed white platelets from alcohol (charcoal) (Found: N, 5·6. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of dinitrile from the pure salt was 76% at 320—390°, one batch of 10 g. gave an 84% yield, and the crude Sandmeyer product one of 80%.

Both these preparations gave the same product, which was also identical with that prepared from potassium 1-chloronaphthalene-2-sulphonate (Cleve, *loc. cit.*). With the technique described above, our yields by the last method were about 30%; like Cook (J., 1932, 459), we were unable to obtain the 60% claimed by Waldmann (*J. pr. Chem.*, 1930, 128, 127). 1 : 2-Dicyanonaphthalene crystallised in white needles, m. p. 190°, from glacial acetic acid, alcohol or petroleum.

5 G. were refluxed for 1½ hours with 70 c.c. of glacial acetic acid, 60 c.c. of concentrated sulphuric acid, and 40 c.c. of water (compare Kay and Morton, J., 1914, 105, 1571). The solution was cooled and poured into water. Naphthalene-1 : 2-dicarboxylic acid was filtered off and purified by dissolution in sodium carbonate solution, reprecipitation, and crystallisation from water; m. p. 176°, yield 71—74%. The anhydride was readily formed by warming the acid (10 g.) with 10 g. of phosphorus pentachloride in 100 c.c. of phosphorus oxychloride until no more hydrogen chloride was evolved. The product was poured into water and filtered, and the anhydride extracted from the residue with benzene. Yield 85%, m. p. 168°, identical with material prepared by Cleve's method (*loc. cit.*). When the anhydride was fused with half its weight of urea, it gave an almost quantitative yield of 1 : 2-naphthalimide, which sublimed in long yellow needles, m. p. 224°, identical with that prepared, following Cleve, from the diamide. The methyl ester, prepared *via* the silver salt, had m. p. 85°, in agreement with Kruber (*Ber.*, 1932, 65, 1382). Methylation of the acid with methyl sulphate in sodium hydroxide solution gave the *methyl hydrogen ester*, m. p. 145° (Found: C, 67·6; H, 4·4. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%). This was also formed by boiling the anhydride with methyl alcohol for a few minutes.

In the following account we shall indicate only those details in which the preparations differed from those of the 1 : 2-series.*

1 : 3-*Series*.—100 G. of commercial 1-aminonaphthalene-3 : 8-disulphonic acid (ε-acid) yielded 20 g. of pure 1-aminonaphthalene-3-sulphonic acid (Found: N, 6·3. Calc.: N, 6·3%) when reduced by Friedländer and Lucht's method (*Ber.*, 1893, 26, 3032). The method of Kalle and Co. (D.R.-P. 64979) was less satisfactory.

Diazotisation followed Royle and Schedler (J., 1923, 123, 1641). The yield of crude *sodium 1-cyanonaphthalene-3-sulphonate* from the Sandmeyer reaction was 100%, 88%. This was difficult to purify. The best method was extraction (Soxhlet) with methyl alcohol, precipitation with ether, and crystallisation from ethyl alcohol (Found: N, 5·9. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of 1 : 3-*dicyanonaphthalene* at 390—400°/100 mm. was 10%, 10% from

* For additional details, see E. F. Bradbrook, Ph.D. Thesis, London (1935).

pure and 9%, 10% from crude sodium cyano-sulphonate. The product crystallised from acetic acid or alcohol in yellow needles. After sublimation and crystallisation from acetic acid it formed white needles, m. p. 170° (Found: C, 80·7; H, 3·4; N, 15·9. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%).

2·5 G. were heated under reflux for 1 hour with 60 c.c. of glacial acetic acid, 10 c.c. of water, and 50 c.c. of concentrated sulphuric acid and the naphthalene-1 : 3-dicarboxylic acid was isolated and purified in the same way as the 1 : 2-acid. Yield, 60% of a pale yellow, amorphous solid, m. p. 267—268°.

1 : 4-*Series*.—1-Naphthylamine-4-sulphonic acid was diazotised, following Erdmann (*loc. cit.*). The Sandmeyer reaction yielded 87% of crude sodium 1-cyanonaphthalene-4-sulphonate (A) as pinkish plates very soluble in water. [If potassium chloride were used in the final salting out, a yield of 81% of crude potassium salt (B) was obtained.] The sodium salt was dissolved in hot water, the solution made just acid with hydrochloric acid, and a slight excess of potassium carbonate added. *Potassium 1-cyanonaphthalene-4-sulphonate* was salted out from the filtered solution by the addition of potassium chloride. It separated from water in small buff crystals (Found: N, 5·4. $C_{11}H_6O_3NSK$ requires N, 5·2%). When fused with potassium ferrocyanide at 320—360°/100 mm., the pure potassium salt gave 71% of 1 : 4-dicyanonaphthalene, the crude potassium salt (B) gave 50%, and the crude sodium salt (A) gave 50%. The dinitrile crystallised from alcohol (charcoal) in long colourless needles, m. p. 208° (Scholl and Neumann, *Ber.*, 1922, 55, 109, give m. p. 208°).

Hydrolysis yielded 94% of naphthalene-1 : 4-dicarboxylic acid, m. p. above 300°. The methyl ester, obtained from the silver salt, crystallised from dilute acetic acid in long white needles, m. p. 67° (Mayer and Sieglitz, *Ber.*, 1922, 55, 120, give m. p. 64°).

1 : 5-*Series*.—Naphthalene-1 : 5-disulphonic acid was purified by Fierz-David's method (*Helv. Chim. Acta*, 1923, 6, 1133). Its barium salt gave 21%, and its sodium salt 12%, of 1 : 5-dicyanonaphthalene when fused with potassium ferrocyanide at 450—550°/50—100 mm.

400 G. of commercial 1-naphthylamine-5-sulphonic acid (Laurent's acid) in 3 l. of hot water were neutralised with sodium carbonate, and the solution filtered and acidified. The precipitated acid was filtered off, washed with hot water, suspended in cold water, and just neutralised with sodium hydroxide. A small amount of sodium 1-naphthylamine-5-sulphonate was removed by filtration, and the filtrate boiled with charcoal and evaporated to dryness. The residual salt was diazotised by Erdmann's method (*loc. cit.*); the damp diazo-compound yielded 85% of crude *sodium 1-cyanonaphthalene-5-sulphonate*, which formed white needles from alcohol (Found: N, 5·6. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of 1 : 5-dicyanonaphthalene was 53% from the pure salt (?) and 50—57% from the crude salt at 330—420° and 40 mm. pressure. It crystallised from glacial acetic acid in white needles, m. p. 268°, not raised by further crystallisation (Scholl and Neumann, *loc. cit.*, give 260°; Moro, *Gazzetta*, 1896, 26, 92, gives 256°). Hydrolysis yielded 70% of the dicarboxylic acid (m. p. above 300°). The methyl ester crystallised from dilute ethyl alcohol in fine long needles, m. p. 110° (Mum, 114—115°; Radcliffe and Short, J., 1931, 220, 113—114°).

1 : 6-*Series*.—Erdmann (*Annalen*, 1893, 275, 210) states that 1 l. of boiling methyl alcohol dissolves 0·9 g. of calcium 1-naphthylamine-6-sulphonate and 13 g. of the 1 : 7-isomeride. Commercial Cleve's acid (1 : 6-, 1 : 7-, and a little 1 : 3-) was neutralised mainly with calcium hydroxide and completely with calcium carbonate. The excess of carbonate was removed, and the solution evaporated to dryness. 100 G. of the calcium salt were extracted (Soxhlet) with 1½ l. of boiling methyl alcohol, until about 5 g. of solid separated from the extract. The extract was filtered and evaporated to dryness, 90 g. of calcium salt, containing mainly the 1 : 7-isomeride, being obtained (A). The residue in the extractor was extracted with fresh methyl alcohol for the same time and finally boiled with 600 c.c. of methyl alcohol to free it completely from the 1 : 7-salt. These extracts were rejected. The calcium salt of the 1 : 6-acid so obtained, treated in the manner described for the 1 : 2-isomeride, yielded 68% of crude sodium 1-cyanonaphthalene-6-sulphonate. The Sandmeyer product contained inorganic matter (cuprous cyanide ?) which could not be removed by crystallisation but was partly eliminated by continuous extraction with methyl alcohol, in which the cyano-sulphonate was more soluble.

Commercial 1-naphthylamine-6-sulphonic acid was suspended in hot water and neutralised with sodium carbonate, and the solution filtered and acidified with hydrochloric acid. The acid which crystallised from the cold solution (100% by titration with standard sodium nitrite) was converted into potassium 1-cyanonaphthalene-6-sulphonate in the usual way. This also contained inorganic impurity and was partly purified as before.

On fusion with potassium ferrocyanide at 340—390°/80 mm. the cyano-sulphonate from the calcium salt gave an 11% yield of dicyanonaphthalene, that from the commercial acid an 18% yield. Neither product was the pure 1 : 6-isomeride and the separation described above was therefore incomplete. Crystallisation from alcohol gave material of m. p. 165—175°; this was extracted with boiling petroleum, and the residue crystallised from glacial acetic acid and sublimed. Pure 1 : 6-dicyanonaphthalene was then obtained as white needles, m. p. 211° (Weissgerber and Kruber, *loc. cit.*, 208—210°). A small amount of what appeared to be crude 1 : 3-isomeride was obtained from the mother-liquors.

Methyl naphthalene-1 : 6-dicarboxylate formed white needles from dilute alcohol, m. p. 97—98° (Meyer and Bernhauer, *Monatsh.*, 1929, 53, 721, 98°).

1 : 7-*Series*.—120 G. of crude calcium 1-naphthylamine-7-sulphonate (such as (A) above) were extracted with boiling methyl alcohol until only about 20 g. remained. The extract yielded, after repetition of this procedure, 80 g. of practically pure 1 : 7-salt, which gave 67 g. of crude sodium 1-cyanonaphthalene-7-sulphonate, contaminated with inorganic impurity. It was partly purified by extraction with alcohol (sample *a*).

A solution of 200 g. of commercial sodium 1-naphthylamine-7-sulphonate in 2 l. of hot water was filtered and acidified with hydrochloric acid. The acid which crystallised on cooling was 90% pure by titration with sodium nitrite. 200 G. yielded 170 g. of crude sodium 1-cyanonaphthalene-7-sulphonate (sample *b*).

Samples *a* and *b* of this salt gave 10% and 30% yields respectively of 1 : *7-dicyanonaphthalene* when fused with potassium ferrocyanide at 340—450°/80 mm. Unlike the 1 : 6-dinitrile, both products were practically free from isomeric impurity. 1 : 7-Dicyanonaphthalene crystallised from alcohol, dilute acetic acid, or light petroleum (b. p. 80—100°) in white needles, m. p. 167° (Found: C, 81·1; H, 3·5; N, 15·8. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%). It gave a 98% yield of the corresponding acid, the methyl ester of which crystallised from dilute alcohol in white plates, m. p. 90° (cf. Ruzicka and van Melsen, *loc. cit.*).

1 : 8-*Series*.—1-Naphthylamine-8-sulphonic acid (*peri*-acid) yielded 77% of crude *sodium 1-cyanonaphthalene-8-sulphonate*. This contained a persistent red impurity, which was removed by repeated crystallisation from a little water, the solution being decolorised with zinc dust and acetic acid (Found: N, 5·3. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The pure salt gave a 9% yield of 1 : *8-dicyanonaphthalene* at 300—400°/80 mm. The dinitrile was best purified by sublimation, followed by crystallisation from alcohol, which yielded white needles, m. p. 232° (Found: C, 81·2; H, 3·0; N, 15·6. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%).

The dinitrile was obtained in rather better yield * by fusing recrystallised potassium 1-cyanonaphthalene-8-sulphonate with an equal weight of dry potassium cyanide for 1 hour at 400°/30 mm. The yield of crude dinitrile was 27%; m. p. 230° after successive crystallisations from alcohol and petroleum (b. p. 100—120°).

On hydrolysis with warm sulphuric acid the dinitrile yielded naphthalic anhydride (long needles from alcohol, m. p. 263°). Methyl naphthalate, made by means of methyl sulphate, formed long needles from dilute methyl alcohol, m. p. 104° (lit., 102—104°).

2 : 6-*Series*.—Sodium 2-naphthylamine-6-sulphonate (100 g., made from commercial Brönner's acid) was suspended in 600 c.c. of water and treated successively with 225 c.c. of concentrated hydrochloric acid and a solution of 30 g. of sodium nitrite in 350 c.c. of water. This diazo-compound was more soluble than its isomerides and the entire liquor from the above was therefore neutralised with sodium carbonate and treated with cuprocyanide solution from 125 g. of copper sulphate and 132 g. of potassium cyanide in 1 l. of water. The addition of 400 g. of sodium chloride liberated crude *sodium 2-cyanonaphthalene-6-sulphonate* (85%), which formed slightly pink plates from water (charcoal) (Found: N, 5·6. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yields of dicyanonaphthalene were 42% from the pure salt and 29% from the crude at 350—450°/50 mm. 2 : 6-Dicyanonaphthalene crystallised from acetic acid (charcoal) in white needles, m. p. 293° (Ebert and Merz, *Ber.*, 1876, 9, 604, give m. p. 297°). The acid obtained on hydrolysis (91% yield, m. p. above 300°), gave through the silver salt a methyl ester, which formed plates from alcohol, m. p. 189° (lit., 187—191°).

2 : 7-*Series*.—Sodium 2-naphthylamine-7-sulphonate (from amino-F-acid), diazotised according to Butler and Royle (J., 1923, 123, 1649), yielded 80% of crude *sodium 2-cyanonaphthalene-7-sulphonate*, which crystallised from concentrated aqueous solution, in the presence of a little zinc and acetic acid, in pale yellow needles (Found: N, 5·5. $C_{11}H_6O_3NSNa$ requires N, 5·5%). 2 : 7-Dicyanonaphthalene was obtained in 7·5% yield from the pure, and 5% yield from the

* This experiment was carried out by Dr. A. R. Lowe.

crude salt at 350—400°/35 mm. After sublimation it crystallised from glacial acetic acid in white needles, m. p. 267°, in agreement with Ebert and Mertz (*loc. cit.*). The methyl ester of the corresponding acid formed long needles from methyl alcohol, m. p. 185°, in agreement with Kaufler and Thien (*Ber.*, 1907, 40, 3258).

2 : 3-*Series* (with A. R. Lowe).—Commercial 2-amino-3-naphthoic acid, purified through the hydrochloride, was diazotised and treated by the Sandmeyer reaction following Waldmann (*loc. cit.*). The product after sublimation had m. p. 279° alone or mixed with 2 : 3-naphthalimide prepared by fusing 2 : 3-naphthalic anhydride with urea (Freund and Fleischer, *loc. cit.*, give m. p. 275° for this imide). 2 : 3-Naphthalimide was sublimed in a rapid stream of ammonia through a hard-glass tube containing thoria electrically heated to 400°. The neutral product was freed from imide and anhydride with caustic alkali and crystallised from alcohol. 2 : 3-*Dicyanonaphthalene* crystallised in shining white needles, m. p. 251° (Found : C, 80·7; H, 3·6; N, 15·8. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 10·7%). Naphthalene-2 : 3-dicarboxylic acid yielded through the silver salt the *methyl* ester, which formed large plates on evaporation of its solution in ether-light petroleum, m. p. 47° (Found : C, 69·3; H, 4·9. $C_{14}H_{12}O_4$ requires C, 68·9; H, 4·9%).

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Imperial College, London, S.W. 7.

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385. *Phthalocyanines. Part VIII. 1 : 2-Naphthalocyanines.*

By E. F. Bradbrook and R. P. Linstead.

The ten dicyanonaphthalenes (preceding paper) have been tested for their ability to form compounds of the phthalocyanine series. The tests (p. 1740) include treatment with various metals, metallic oxides and chlorides. 1 : 2- and 2 : 3-Dicyanonaphthalene combine readily with a number of metallic reagents to yield green colouring matters; the other isomerides show no reaction whatever. The green compounds derived from 1 : 2-dicyanonaphthalene are of the phthalocyanine type and the behaviour of its isomerides thus verifies the statement that "the two nitrile groups participating in phthalocyanine formation must be linked to adjacent carbon atoms of an aromatic nucleus" (Dent, Linstead, and Lowe, J., 1934, 1034). It is of particular interest that 1 : 8-dicyanonaphthalene yields no such compounds, although the corresponding acid resembles phthalic acid in many respects. It is, however, impossible for this dinitrile to yield a compound of the type of phthalocyanine, on the basis of the formula proposed for the latter (*loc. cit.*).

Owing to the comparative inaccessibility of 2 : 3-dicyanonaphthalene we have confined our attention to the 1 : 2-isomeride. The parent acid being regarded as 1 : 2-naphthalic acid, the derived pigments are conveniently named 1 : 2-naphthalocyanines, more strictly tetra-3 : 4-benzphthalocyanines (see I). Preliminary experiments with a number of metals showed that the *copper*, *magnesium*, *zinc*, and *lead* derivatives were very easily formed.* Copper and zinc react with 1 : 2-dicyanonaphthalene at 270—300°, *i.e.*, a rather higher temperature than that necessary for the corresponding reaction with phthalonitrile. The reaction is exothermic, but less so than in the simpler series. Magnesium reacts only at the boiling point of the nitrile (370°). The lead derivative is prepared from litharge and the dinitrile, like the corresponding phthalocyanine. The products are obtained in good yields as rather dark green masses with a purple to blue lustre; there is no appreciable side reaction.

The metallic naphthalocyanines show little tendency to sublime, probably on account of their very large molecular weight, but can be purified by crystallisation from suitable high-boiling solvents. They are rather more soluble than the phthalocyanines, but, unlike the latter, do not crystallise well. Magnesium 1 : 2-naphthalocyanine is exceptional;

* Our thanks are due to Dr. A. R. Lowe for carrying out a number of preliminary experiments in both the 1 : 2- and the 2 : 3-series.

two isomeric forms have been isolated, one of which (α-form) is freely soluble in cold ether and has been obtained macrocrystalline.

Analysis of the purified metallic compounds shows them to have the general formula $(C_{12}H_6N_2)_4M$, where M is a bivalent metal. The compounds are therefore simply related to the known metallic phthalocyanines $(C_8H_4N_2)_4M$, in agreement with the close resemblance between their physical and chemical properties.

The stability of the metals towards concentrated sulphuric acid is also analogous. Zinc and copper naphthalocyanines give purple solutions which regenerate the unchanged compounds on dilution. On the other hand the lead and α-magnesium compounds are decomposed, the metal is eliminated, and free 1 : 2-*naphthalocyanine*, $(C_{12}H_6N_2)_4H_2$, is formed. When this is boiled with metals in chloronaphthalene, it regenerates the metallic derivatives.

The 1 : 2-naphthalocyanines show an even greater general stability to heat and reagents than the phthalocyanines. In particular they are only slowly oxidised by nitric acid or ceric sulphate. On this account it has not been possible to prove the presence of two oxidisable hydrogen atoms in free naphthalocyanine by quantitative oxidation (Dent, Linstead, and Lowe, *loc. cit.*). α-Magnesium naphthalocyanine, however, is more readily attacked and the oxygen uptake from cold acid ceric sulphate agrees approximately with that required for the equation

$$(C_{12}H_6N_2)_4Mg + 8H_2O + O = 4C_{12}H_7O_2N + 4NH_3 + MgO$$

1 : 2-Naphthalimide and ammonium sulphate are formed. This proves that the metal is combined in the same manner in the 1 : 2-naphthalocyanines as in the phthalocyanines.

The parallelism between the two series also appears in the reaction between cupric chloride and 1 : 2-dicyanonaphthalene (cf. Dent and Linstead, J., 1934, 1027). These react exothermically at 200° with the formation of hydrogen chloride and *copper chloro-1 : 2-naphthalocyanine* :

$$CuCl_2 + 4C_{12}H_6N_2 = (C_{12}H_6N_2)_3Cu(C_{12}H_5ClN_2) + HCl$$

When the product was decomposed with concentrated nitric and sulphuric acids, all the chlorine appeared in the organic fission product and no chloride ion was formed. This shows that the chlorine is nuclear, but its position is unknown.

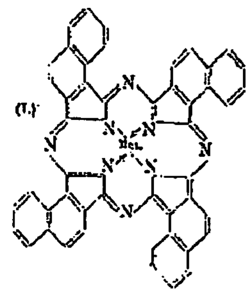
The most interesting feature of the series lies in the existence of isomerides, which was first noticed in the case of the magnesium compound. The crude product of the interaction of magnesium and 1 : 2-dicyanonaphthalene is a mixture of a bright green, ether-soluble α-form and a dark green, insoluble β-form in the ratio 2·5 : 1. The α-form does not form a hydrate, although the unusual solubility in ether, acetone and ethyl acetate indicates a tendency to solvation. The β-form is normally isolated as the *monohydrate*, which loses its water at 215°. The anhydrous form readily regains one molecule of water, but there is no tendency for the formation of a dihydrate as with magnesium phthalocyanine. Like the α-isomeride, the β-magnesium compound yields 1 : 2-naphthalimide on oxidation with ceric sulphate. The two magnesium compounds yield *two different metal-free compounds* on treatment with sulphuric acid. When these are heated with magnesium, they regenerate the isomeric α- and β-magnesium derivatives severally : hence there is a persistent structural difference between the two series.

The β-form of free naphthalocyanine is rather darker than the ordinary α-form, but does not show any marked difference in solubility. The free naphthalocyanine prepared from lead naphthalocyanine appears to be identical with the α-isomeride. Moreover, treatment of the α-magnesium derivative with either copper or zinc in boiling chloronaphthalene leads by an exchange of metal to the formation of copper and zinc naphthalocyanines, indistinguishable from those prepared directly from 1 : 2-dicyanonaphthalene. It appears that either the other metallic derivatives all belong to the α-series or their α- and β-modifications are not clearly distinguishable. Slight variations in solubility were indeed noticed, but insufficient for separation.

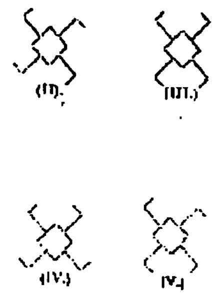
For the interpretation of this isomerism we may take as proved the structural analogy

between 1 : 2-naphthalocyanines and phthalocyanines. Four formulæ for the metal-free or metallic derivatives then become possible, one of which is shown in full :

(I.)



(II.) (III.) (IV.) (V.)



If we represent the large ring as a lozenge and the aromatic rings by straight lines, this formula may be conveniently symbolised by (II) and the three other possible isomerides by (III), (IV), and (V). The isomerism thus depends upon the relative positions of the four outer benzene rings. We tentatively assign the most symmetrical "swastika" formula (I and II) to the common α-series. The β-series may correspond to one of (III), (IV), and (V) or to a mixture of all three.

It is instructive to compare the easily crystallisable phthalocyanines, which cannot exhibit this isomerism, with the naphthalocyanines, which may be isomeric mixtures and cannot be obtained crystalline except in one case (α-magnesium) where the separation of the mixture is especially easy.

Experimental.

Tests on Dicyanonaphthalenes.—For conversion into substances of the phthalocyanine type, the dinitrile was heated with sodium, sodium ethoxide, sodium amyloxide, magnesium, magnesium oxide, copper-bronze, cuprous chloride, anhydrous cupric chloride, anhydrous zinc chloride, and anhydrous ferric chloride. The 1 : 2- and the 2 : 3-dinitrile gave positive results (green colour, violet reflex) with all these reagents.

General Notes on the Analysis of 1 : 2-Naphthalocyanines.—In carbon and hydrogen analyses the burning was complete in 15—20 minutes. Nitrogen estimations were made by the Kjeldahl method, the Dumas method being unsatisfactory owing to the stability of the compounds in the inert atmosphere. Chlorine was determined by Liebig's method. Zinc and magnesium were estimated by ignition to the oxides. Copper in copper chloronaphthalocyanine was determined by oxidation of about 0·2 g. with 20 c.c. of concentrated sulphuric acid and a few drops of nitric acid, concentration to 2 c.c., and dissolution in water. The solution was then neutralised with ammonia, barely acidified with hydrochloric acid, and filtered. The filtrate was reduced with sulphur dioxide, and warmed for 1 hour with an excess of ammonium thiocyanate. After standing overnight, the cuprous thiocyanate was weighed in the usual way. Lead was estimated by boiling the pigment (0·4 g.) with concentrated nitric acid until it was destroyed (2 days). The colourless solution was diluted to 200 c.c., boiled, cooled, and filtered. The filtrate and washings were neutralised with ammonia, made slightly acid with nitric acid, and diluted to 600 c.c. The lead was precipitated as chromate and weighed in the usual manner. Micro-analyses by Schoeller are asterisked.

Copper (with A. R. Lowe; compare also B.P. 410,814).—3 G. of 1 : 2-dicyanonaphthalene were heated with 1 g. of reduced copper for 1 hour at 260—260° by means of a mixed nitrate bath. From the cold powdered melt, boiling alcohol extracted 1·75 g. of unreacted dinitrile. The residue was dissolved in cold concentrated sulphuric acid, and the dark purple solution poured on ice. The green precipitate was filtered off, and washed with hot water (until free from acid), alcohol and ether. Yield, 46%. Two crystallisations from quinoline yielded pure *copper 1 : 2-naphthalocyanine* as a green mass with a violet reflex (Found : C, 74·0; H, 3·7; N, 14·3; Cu, 8·0. $C_{48}H_{24}N_8Cu$ requires C, 74·3; H, 3·1; N, 14·5; Cu, 8·2%). The pure compound

dissolved in sulphuric acid to give a blue solution, from which it was regenerated almost quantitatively on dilution.

10 G. of the dinitrile and 2·1 g. (1¼ mols.) of anhydrous cupric chloride were heated to 260—270°; hydrogen chloride and heat were evolved and the melt solidified in 8 minutes. It was heated for a further 20 minutes at 280—290° and the green product was then extracted with water and boiling benzene. Yield of residue, 87%. Two crystallisations from chloronaphthalene gave *copper chloro-1 : 2-naphthalocyanine*, similar in appearance to the unchlorinated compound (Found : C, 70·7; H, 2·8; N, 13·7; Cl, 4·8; Cu, 8·0. $C_{48}H_{23}N_8ClCu$ requires C, 71·1; H, 2·8; N, 13·8; Cl, 4·4; Cu, 7·9%). The chlorine was not removed by boiling sodium hydroxide solution. 0·85 G. of the compound was dissolved in 50 c.c. of concentrated sulphuric acid, and a few drops of nitric acid added. The yellow solution yielded 0·7 g. of pale yellow solid when poured on ice, but no chloride ion. The solid melted at 250—260° after crystallisation from acetic acid and contained chlorine, but was not identified.

Zinc.—10 G. of 1 : 2-dicyanonaphthalene and 1 g. of zinc dust were heated at 275° for 20 minutes and at 310—320° for a further ½ hour. Recovery of dinitrile, 2·3 g. Yield, 7·3 g. of a green powder with a purple lustre, containing excess of zinc. The product was slightly soluble in ether, ethyl acetate, chlorobenzene and toluene, more so in quinoline, aniline and chloronaphthalene. It was crystallised from the last-named solvent [Found : (for twice crystallised material) C, 74·0; H, 3·2; Zn, 8·3; (for thrice crystallised) C, 74·0; H, 3·2; N, 14·4; Zn, 8·4. $C_{48}H_{24}N_8Zn$ requires C, 74·1; H, 3·1; N, 14·4; Zn, 8·4%]. The solution in sulphuric acid was purple and regenerated the compound almost quantitatively on dilution.

Lead.—1 : 2-Dicyanonaphthalene (18 g.) reacted vigorously with litharge (0·8 g., 1¼ mols.) at 275—280°. The mass was almost solid in 5 minutes and was heated for a further 20 minutes. The recovery of dinitrile was 3·0 g.; the yield of pigment 20·3 g., containing the excess of litharge.

Lead 1 : 2-naphthalocyanine was yellowish-green with a blue lustre. It was soluble in hot pyridine, quinoline, chlorobenzene, and chloronaphthalene and was crystallised from aniline (Found : C, 63·25, 63·1*; H, 2·9, 3·0*; N, 12·8; Pb, 21·7. $C_{48}H_{24}N_8Pb$ requires C, 62·7; H, 2·6; N, 12·2; Pb, 22·6%). 1 G. was treated with sulphuric in the usual way. Dilution yielded 0·85 g. of 1 : 2-*naphthalocyanine* contaminated with lead sulphate, from which aniline extracted the pure metal-free compound (Found : C, 80·4; H, 3·7; ash, negligible. $C_{48}H_{26}N_8$ requires C, 80·7; H, 3·6%). It was identical in appearance with the α-1 : 2-naphthalocyanine described below.

Magnesium and Metal-free Compounds.—After preliminary experiments the following procedure was adopted. 40 G. of 1 : 2-dicyanonaphthalene and 2·1 g. of etched magnesium turnings were heated at 305—370° for 80 minutes, the mass then being almost solid. The unreacted dinitrile was extracted with benzene, and the residue ground with water (this converted all the β-magnesium compound into the monohydrate, which is insoluble in ether, whereas the anhydrous β-compound appears to be slightly soluble). The product was dried and exhaustively extracted with ether (Soxhlet). Evaporation of the solution gave α-*magnesium 1 : 2-naphthalocyanine* as a fairly bright green mass with a fine purple lustre. A small amount of 1 : 2-dicyanonaphthalene present as impurity was sublimed out at 230—240° in a stream of carbon dioxide under reduced pressure. The β-*magnesium 1 : 2-naphthalocyanine* left in the extractor was sifted from excess of magnesium and again boiled with benzene. Average yields, 62% of α- and 24% of β-compound.

α-Magnesium 1 : 2-naphthalocyanine was soluble in ethyl alcohol, acetone, ethyl acetate, and chloroform and extremely soluble in ether. It was purified by two extractions with cold ether, filtration, and evaporation to dryness (Found : C, 78·3; H, 3·4; N, 15·1; Mg, 3·3. $C_{48}H_{24}N_8Mg$ requires C, 78·3; H, 3·3; N, 15·2; Mg, 3·3%). The β-isomeride was purified by two crystallisations from chloronaphthalene. Three separate preparations were analysed (Found : C, 76·4, 76·8, 76·7; H, 3·5, 3·4, 3·5; Mg, 2·9, 3·0. $C_{48}H_{24}N_8Mg,H_2O$ requires C, 76·4; H, 3·5; Mg, 3·2%).

1 G. of the α-compound was dissolved in 75 c.c. of concentrated sulphuric acid, and the purple solution filtered and poured on washed ice. The α-1 : 2-*naphthalocyanine* was washed with hot water, alcohol, and ether. Yield, 0·8 g. of a green solid with a purple lustre. It was soluble in boiling aniline but not in ether and the other low-boiling solvents which dissolved the α-magnesium compound (Found : C, 80·0; H, 3·8; N, 15·0; ash, negligible. $C_{48}H_{26}N_8$ requires C, 80·7; H, 3·6; N, 15·7%). 0·7 G. of the β-magnesium compound on similar treatment gave 0·5 g. of β-1 : 2-*naphthalocyanine*, darker green than the α-isomeride and with a purple lustre (these colours were conveniently compared as rubbings on glazed paper). It

was purified by crystallisation from chloronaphthalene (Found : C, 81·0; H, 3·7%; ash, negligible).

It seemed possible that the metal of the α-magnesium compound might be eliminated by passing dry hydrogen chloride through an ethereal solution. Experiment showed that after 2 hours the pigment was completely precipitated but only about 10% of the metal had been removed. The precipitation was caused by the formation of the oxonium compound between the ether and the hydrogen chloride, since α-magnesium naphthalocyanine was insoluble in ether saturated with the gas but dissolved when such a suspension was shaken with water.

Reactions of the Magnesium Compounds.—Metal exchange. 3 G. of α-magnesium 1 : 2-naphthalocyanine and 1 g. of reduced copper were refluxed for 31 hours in 75 c.c. of chloronaphthalene. No trace of the magnesium compound remained and the product after crystallisation from chloronaphthalene yielded pure copper 1 : 2-naphthalocyanine, identical in colour and reflex with that prepared directly from 1 : 2-dicyanonaphthalene (Found : C, 74·3; H, 3·3; Cu, 8·2%). A similar experiment with metallic zinc showed that in 7 hours about 40% of the magnesium was replaced by zinc.

Oxidation. The finely divided α-magnesium compound was heated with ceric sulphate solution until the colour was destroyed. The solution deposited 1 : 2-naphthalimide (75—80%) on standing, m. p. and mixed m. p. 224° after sublimation. A considerable excess of the theoretical amount of ceric sulphate was used up. 0·336 G. of the powdered α-magnesium compound was left in the cold for 5 days with 20 c.c. of 0·0480N-ceric sulphate. The yellow product was filtered from naphthalimide, and the excess of ceric sulphate estimated with ferrous ammonium sulphate in the usual way (Dent, Linstead, and Lowe, *loc. cit.*). 12·4 C.c. of ceric sulphate solution were used in the oxidation, equivalent to 1·3 atoms of oxygen per molecule (calc., 1·0).

0·5 G. of the β-magnesium compound was oxidised qualitatively in the same manner as the α-isomeride. Yield of 1 : 2-naphthalimide, 0·25 g., m. p. and mixed m. p. 224°.

Dehydration. The β-magnesium compound attained constant weight after 4 hours in a vacuum at 210—220°, the loss in weight being 2·1% (calc., 3·4%). The moisture was regained rapidly in the air and was again lost at 215°. Two separately dehydrated samples were analysed; a little hydration occurred during weighing (Found : C, 77·3, 77·4; H, 3·4, 3·4. $C_{48}H_{24}N_8Mg$ requires C, 78·3; H, 3·3%).

Reactions of the Free 1 : 2-Naphthalocyanines.—1 G. of α-naphthalocyanine was refluxed with granulated zinc in 30 c.c. of chloronaphthalene for 7½ hours. The pigment was purified through sulphuric acid. Analysis showed that a 40% conversion into zinc naphthalocyanine had occurred and this was practically complete after a further 24 hours' treatment. A similar reaction was performed with magnesium (24 hours), the chloronaphthalene being removed with benzene. From the residue, ether extracted the α-magnesium compound (1·3 g. from 2 g. of α-naphthalocyanine). The small portion insoluble in ether was probably the unreacted metal-free compound, but may have contained some β-magnesium compound (see below).

1·1 G. of β-1 : 2-naphthalocyanine were refluxed for 10 hours with 0·2 g. of magnesium in 40 c.c. of chloronaphthalene. The product was boiled with benzene, and the residue allowed to stand with water. Extraction with cold ether removed 0·07 g. of soluble material which appeared to be the α-magnesium derivative. The bulk of the product was insoluble (0·85 g.) and yielded the β-magnesium compound as the monohydrate after crystallisation from chloronaphthalene and standing with water (Found : C, 75·1; H, 3·0; Mg, 3·0. Calc. for $C_{48}H_{24}N_8Mg,H_2O$: C, 76·1; H, 3·5; Mg, 3·2%).

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386. *The Action of Sodium Nitrite on* p-*Nitrodimethylaniline in Hydrobromic Acid.*

By GEORGE J. G. MILTON and THOMAS H. READE.

BROMINATION in the 2-position occurs when *p*-nitrodimethylaniline is treated with hydrobromic acid and nitrous acid at 0°, the excess acid being 5N. The brown substance precipitated is a *perbromide* of 2-bromo-4-nitrodimethylaniline hydrobromide, the orientation of which was established by Norton and Allen (*Ber.*, 1885, 18, 1995). 2-Bromo-4-nitrodimethylaniline perbromide, treated with hot aqueous alcohol, gives *2-bromo-4-nitrodimethylaniline*, which with sodium nitrite in dilute hydrochloric acid forms *2-bromo-4-nitrophenylmethylnitrosamine*. Elimination of the nitroso-group by hot concentrated hydrochloric acid yields *2-bromo-4-nitromethylaniline*, which on nitration with nitric acid (d 1·43) gives 2-bromo-4 : 6-*dinitrophenylmethylnitrosamine*; this, when boiled with phenol and water, is converted into 2-bromo-4 : 6-dinitromethylaniline.

To ascertain at what concentration of hydrogen bromide mixtures of nitrous and hydrobromic acids act as a brominating agent, small quantities of phenyltrimethylammonium bromide were added to the nitrous-hydrobromic acid mixtures. Above 0·36N the orange perbromide $NPhMe_3Br_3$ was precipitated, solutions 0·305—0·358N were cloudy, and solutions weaker than 0·3N remained clear.

The limiting bromine concentration is about 0·000 gram-mol. per litre as detected by formation of perbromide. The presence of alkali bromide or hydrobromic acid diminishes this sensitivity to about one half when the ratio of bromide to bromine is 5. This observation is significant, because the perbromide dissolves less easily in solutions containing small amounts of bromides than it does in water alone. The precipitated perbromide passes into solution at the rate of about ½ gram in 24 hours. The dissolution is accompanied by decomposition, during which a part of the bromine escapes by volatilisation, a part enters the benzene nucleus in the *m*-position with formation of hydrogen bromide, and only a small amount is available to liberate iodine from slightly acidified potassium iodide. The greater part of the bromine, however, is probably present as bromate (the production of which takes place as readily in nitrogen as in air), for the solution, after being warmed with concentrated hydrochloric acid and diluted, liberates 0·4 equiv. of iodine from potassium iodide. As a check on the value 0·3N below which no bromine was liberated in the hydrobromic-nitrous acid mixtures, air or carbon dioxide was aspirated through the mixtures at 0° into acidified silver nitrate solutions for 6 hours. Experiments in which the sodium nitrite was omitted, or sodium nitrate was used instead of sodium nitrite, gave no silver bromide below a hydrogen bromide concentration of 7·25N.

EXPERIMENTAL.

Perbromide of 2-Bromo-4-nitrodimethylaniline Hydrobromide.—This *substance* was precipitated as a dark brown powder when sodium nitrite (4 mols.) in a little water was added at 0° to *p*-nitrodimethylaniline (1 mol.) dissolved in hydrobromic acid of concentration exceeding 4N. After recrystallisation from glacial acetic acid, it formed brown plates, m. p. 157°, soluble in ether, acetone, hot ethyl alcohol, or concentrated mineral acids (with decomp.). When wetted, the substance liberated iodine from starch–iodide paper (Found : C, 19·8; H, 1·85; N, 5·9; Br (ionisable), 49·5; Br (total), 60·0. $C_8H_{11}O_2N_2Br_4$ requires C, 19·9; H, 2·05; N, 5·8; Br (ionisable), 49·0; Br (total), 66·1%).

2-Bromo-4-nitrodimethylaniline.—When the perbromide was heated with aqueous alcohol, this *substance* crystallised in yellow needles, m. p. 74°, soluble in ether, acetone, or hot alcohol, not easily soluble in dilute acids, but moderately readily soluble in cold concentrated acids (Found : C, 39·2; H, 3·7; N, 11·4; Br, 32·65. $C_8H_9O_2N_2Br$ requires C, 39·1; H, 3·6; N, 11·4; Br, 32·8%).

2-Bromo-4-nitrophenylmethylnitrosamine was precipitated in a few hours at 0° from a hydrochloric acid solution of the tertiary amine on addition of sodium nitrite (3 mols.). After crystallisation from alcohol, it formed nearly white needles, m. p. 95°, which gave the Liebermann reaction for nitroso-compounds, were little soluble in strong acids, but dissolved in ether,